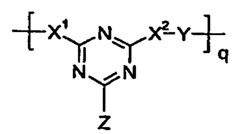
Novel Polymers for Use in Optical Devices

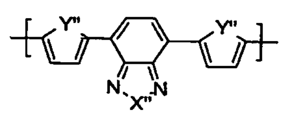
The present invention relates to novel polymers comprising benzotriazol containing repeating units and to their use in optical devices, such as an optical device comprising an electroluminescent device or a photovoltaic device.

Derivatives of poly(p-phenylenevinylene) have been known for some time as electroluminescence (EL) materials (see, for example, WO90/13148).

WO98/11150 discloses triazine polymers of formula  and their use in electroluminescence (EL) arrangements.

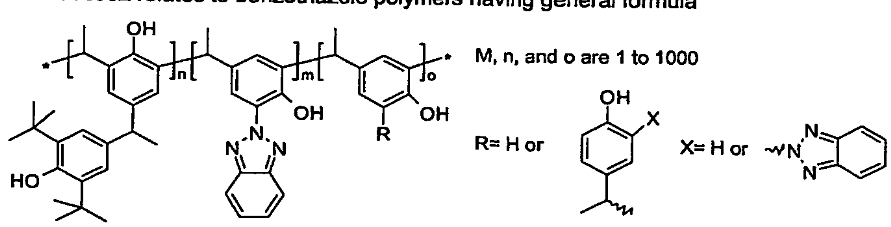
WO00/46321 and US-B-6,512,083 relate to fluorene-containing polymers and their use in EL arrangements.

WO01/49768 discloses luminescent polymers comprising a triarylene repeat unit which comprises a triarylene of general formula



which is substituted or unsubstituted and an arylene repeat unit -[-Ar-]- that is different from the triarylene repeat unit wherein X" and Y" are each independently O, S, CR, SiR or NR and each R is independently alkyl, aryl or H.

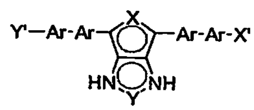
WO97/12882 relates to benzotriazole polymers having general formula



which are useful as ultraviolet light stabilizers and metal chelaters. The products of

WO97/12882 are derivatives of 4-hydroxyacetophenone benzotriazole and 4-hydroxyphenylmethyl carbinol benzotriazole.

WO02/059121 relates to monomers having general formula



, which may be substituted or unsubstituted: where X' and Y' are the same or different and are reactive groups capable of undergoing chain extension; X is O, S, NR, RC-CR or RC=CR; Y is O, S, NR, RC-CR or RC=CR; R is H or a substituent group; and Ar is a substituted or unsubstituted aryl or heteroaryl group.

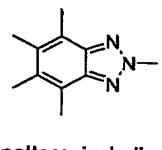
There are a number of challenges faced with the introduction of organic EL displays when their performance is compared with existing technologies. Obtaining the exact color coordinates required by specific guidelines (i.e. NTSC) has been problematic. The operational lifetime of the EL device is relatively lower when contrasted to the existing inorganic technology. In addition, producing a material with a pure blue color and a long lifetime is one of the greatest problems for this industry.

Accordingly, it is the object of the present invention to provide novel materials, which show significant advantages in color purity, device efficiency and/or operational lifetime, when incorporated in optical devices.

Said object is solved by the polymers of the present invention comprising benzotriazole containing repeating units. Optical devices, comprising the polymers of the present invention, can show significant advantages in color purity, device efficiency and/or operational lifetime. In addition, the polymers can have good solubility characteristics and relatively high glass transition temperatures, which facilitates their fabrication into coatings and films that are relatively thin, thermally stable, and relatively free of defects. If the polymers contain end groups which are capable of being crosslinked, the crosslinking of such groups after the films or coating is formed increases the solvent resistance thereof, which is beneficial in applications wherein one or more solvent-based layers of material are deposited thereon.

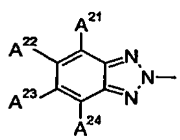
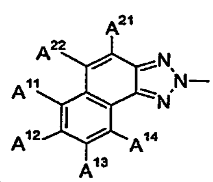
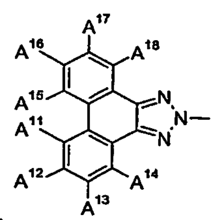
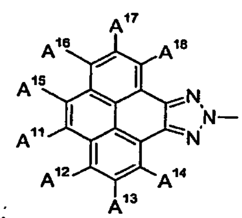
Accordingly, the polymers of the present invention should have a glass transition temperature above 100°C, especially a glass transition temperature above 150°C.

The repeating units of the polymers of the present invention comprise a benzotriazole backbone

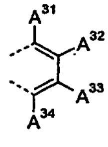
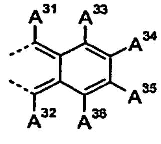


, wherein the phenyl group of the benzotriazole may be substituted in any pattern, including fused ring systems. The benzotriazole monomer (or comonomer) may give rise to a main-chain or a pendant structure of the polymer, both of which may be conjugated or non-conjugated. The present invention is not limited to a benzotriazole structure where one connection to the polymer is through the phenyl ring or a group attached thereto and the other is through the substituent attached to the nitrogen atom. Other structures may exist where both links to the polymer chain are on the the phenyl ring or a group attached thereto, and similarly, where both polymer connections are on the substituent attached to the nitrogen atom. In addition, the benzotriazole moiety may be connected to a polymer in a pendant manner.

Examples of the benzotriazole backbones are groups of the following formula

 ,  ,  ; 

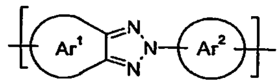
wherein A^{21}, A^{22}, A^{23}, A^{24}, A^{11}, A^{12}, A^{13}, A^{14}, A^{15}, A^{16}, A^{17} and A^{18} are independently of each other H, halogen, SO_3^-, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_1-C_{18}perfluoroalkyl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or -CO-R^{28}, wherein E, D, G and R^{28} are defined as below, or

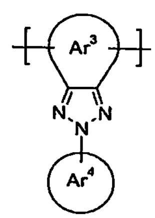
two groups A^{11}, A^{12}, A^{13}, A^{14}, A^{15}, A^{16}, A^{17} and A^{18}, which are neighbouring to each other, are a group  , or  , wherein A^{31}, A^{32}, A^{33}, A^{34}, A^{35}, A^{36} and A^{37} are

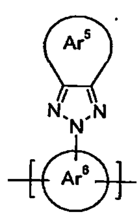
independently of each other H, halogen, SO_3^-, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_1-C_{18}perfluoroalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or -CO-R^{28}, and up to 2 substituents A^{21}, A^{22}, A^{23}, A^{24}, A^{11}, A^{12}, A^{13}, A^{14}, A^{15}, A^{16}, A^{17}, A^{18}, A^{31}, A^{32}, A^{33}, A^{34}, A^{35}, A^{36} and A^{37} can represent the connection to the polymer.

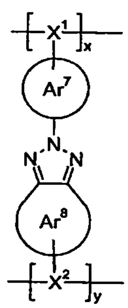
As used herein the term "polymer of the present invention" refers to polymers having repeating units of formula I, including formula Ia to Id, II, including formula IIa to IIg, formula III, and/or formula IV, including formula IVa to IVc.

Accordingly, the present invention relates to polymers comprising a repeating unit of the formula


(I),


(II),


(III), or

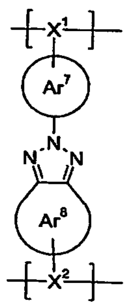

(IV), wherein

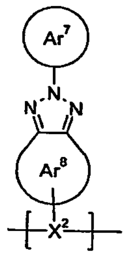
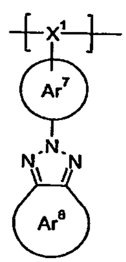
x and y are 0 or 1,

X^1 and X^2 are independently of each other a divalent linking group,

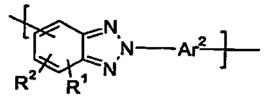
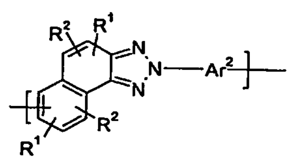
Ar^1, Ar^2, Ar^3, Ar^4, Ar^5, Ar^6, Ar^7 and Ar^8 are independently of each other an aryl group, or a heteroaryl group, which can optionally be substituted, especially a C_6-C_{30}aryl group, or a C_2-C_{26}heteroaryl group, which can optionally be substituted.

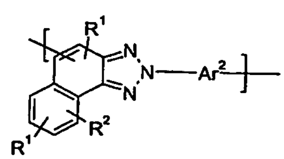
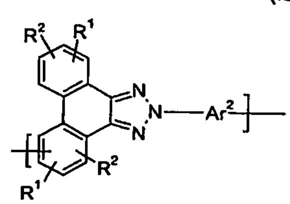
In the repeating units of formula IV at least one of x and y is 1. If x and y are both 1,

repeating units of formula  (IVc) results, which could be seen as a "crosslinking structure", present in 0.01-3 %. Preferred are, however, repeating units of formula

 (IVa) and  (IVb).

Among the repeating units of the formula I, repeating units of formula

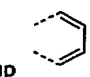
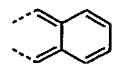
 (Ia),  (Ib),

 (Ic), or  (Id) are preferred,

wherein Ar^2 is as defined above,

R^1 and R^2 are independently of each other H, halogen, SO_3^-, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_1-C_{18}perfluoroalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl,

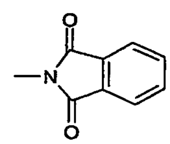
C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or -CO-R^{28},

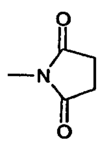
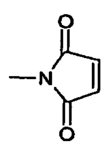
or two substituents R^1 and R^2, which are adjacent to each other, are a group , or ,

D is -CO-; -COO-; -S-; -SO-; -SO_2-; -O-; -NR^{25}-; -$SiR^{30}R^{31}$-; -POR^{32}-; -CR^{23}=CR^{24}-; or -C≡C-; and

E is -OR^{29}; -SR^{29}; -$NR^{25}R^{26}$; -COR^{28}; -$COOR^{27}$; -$CONR^{25}R^{26}$; -CN; -$OCOOR^{27}$; or halogen; G is E, or C_1-C_{18}alkyl, wherein

R^{23}, R^{24}, R^{25} and R^{26} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-; or

R^{25} and R^{26} together form a five or six membered ring, in particular ,

, or ,

R^{27} and R^{28} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-,

R^{29} is H; C_6-C_{18}aryl; C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-,

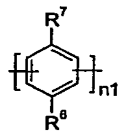
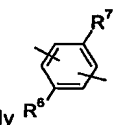
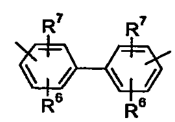
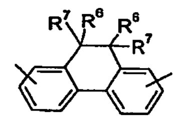
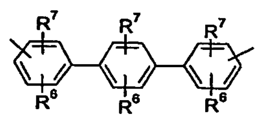
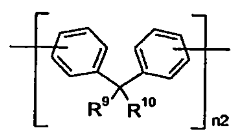
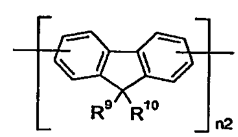
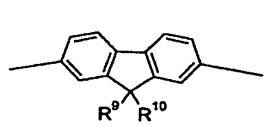
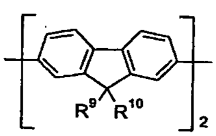
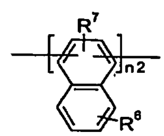
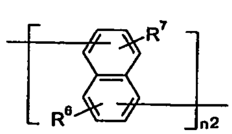
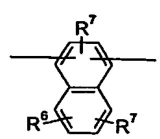
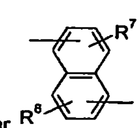
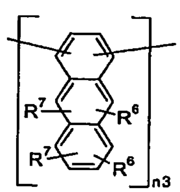
R^{30} and R^{31} are independently of each other C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, and

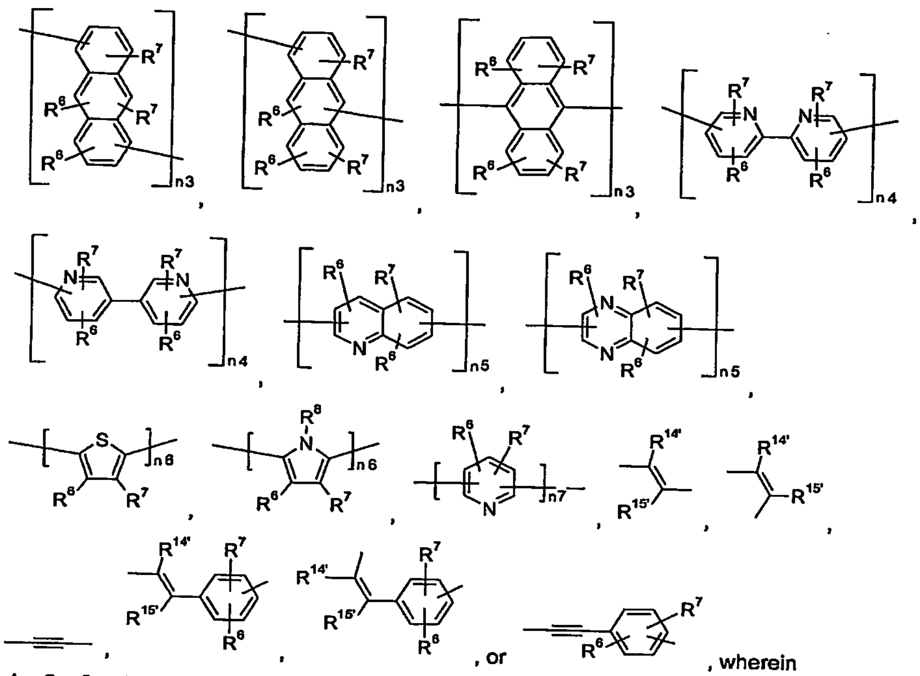
R^{32} is C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl.

Preferably, R^1 and R^2 are independently of each other H, C_1-C_{18}alkyl, such as as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, or sec-butyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl.

D is preferably -CO-, -COO-, -S-, -SO-, $-SO_2-$, -O-, $-NR^{25}-$, wherein R^{25} is C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, or sec-butyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl.

E is preferably $-OR^{29}$; $-SR^{29}$; $-NR^{25}R^{25}$; $-COR^{28}$; $-COOR^{27}$; $-CONR^{25}R^{25}$; or -CN; wherein R^{25}, R^{27}, R^{28} and R^{29} are independently of each other C_1-C_{18} alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, or C_6-C_{24} aryl, such as phenyl, naphthyl, or biphenyl.

Examples of Ar^2 are a single bond, -CO-, -COO-; -S-; -SO-; $-SO_2-$; -O-; $-CR^{23}=CR^{24}-$; or -C≡C-; especially , especially , , , , , , especially , or ; , , especially , or ; ,



, wherein

n1, n2, n3, n4, n5, n6 and n7 are integers of 1 to 10, in particular 1 to 3,

R^6 and R^7 are independently of each other H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or -CO-R^{28},

R^8 is C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24} aryl, or C_7-C_{25}aralkyl,

R^9 and R^{10} are independently of each other C_1-C_{18} alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, or C_7-C_{25}aralkyl, or

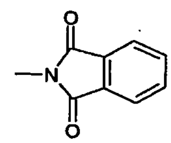
R^9 and R^{10} form a ring, especially a five- or six-membered ring,

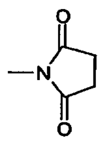
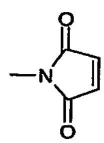
$R^{14'}$ and $R^{15'}$ are independently of each other H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G,

D is -CO-; -COO-; -S-; -SO-; -SO_2-; -O-; -NR^{25}-; -$SiR^{30}R^{31}$-; -POR^{32}-; -CR^{23}=CR^{24}-; or -C≡C-; and

E is $-OR^{29}$; $-SR^{29}$; $-NR^{25}R^{26}$; $-COR^{28}$; $-COOR^{27}$; $-CONR^{25}R^{26}$; -CN; $-OCOOR^{27}$; or halogen; G is E, or C_1-C_{18}alkyl, wherein

R^{23}, R^{24}, R^{25} and R^{26} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-; or

R^{25} and R^{26} together form a five or six membered ring, in particular ,

, or ,

R^{27} and R^{28} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-,

R^{29} is H; C_6-C_{18}aryl; C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-,

R^{30} and R^{31} are independently of each other C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, and

R^{32} is C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl.

Preferably, R^6 and R^7 are independently of each other H, C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, such as $-CH_2OCH_3$, $-CH_2OCH_2CH_3$, $-CH_2OCH_2CH_2OCH_3$, or $-CH_2OCH_2CH_2OCH_2CH_3$, C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl, C_6-C_{24}aryl which is substituted by G, such as $-C_6H_4OCH_3$, $-C_6H_4OCH_2CH_3$, $-C_6H_3(OCH_3)_2$, or $-C_6H_3(OCH_2CH_3)_2$, $-C_6H_4CH_3$, $-C_6H_3(CH_3)_2$, $-C_6H_2(CH_3)_3$, or $-C_6H_4tBu$.

R^8 is preferably H, C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, n-heptyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl.

Preferably, R^9 and R^{10} are independently of each other H, C_1-C_{18}alkyl, such as n-butyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by

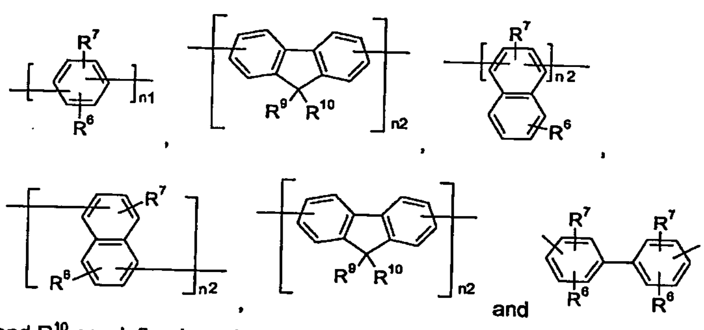
D, such as $-CH_2(OCH_2CH_2)_wOCH_3$, w = 1, 2, 3, or 4, C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl, C_6-C_{24}aryl which is substituted by G, such as $-C_6H_4OCH_3$, $-C_6H_4OCH_2CH_3$, $-C_6H_3(OCH_3)_2$, $-C_6H_3(OCH_2CH_3)_2$, $-C_6H_4CH_3$, $-C_6H_3(CH_3)_2$, $-C_6H_2(CH_3)_3$, or $-C_6H_4tBu$, or R^9 and R^{10} together form a 4 to 8 membered ring, especially a 5 or 6 membered ring, such as cyclohexyl, or cyclopentyl.

Preferably, $R^{14'}$ and $R^{15'}$ are independently of each other H, C_1-C_{18}alkyl, such as as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, or sec-butyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl.

D is preferably -CO-, -COO-, -S-, -SO-, $-SO_2-$, -O-, $-NR^{25}-$, wherein R^{25} is C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, or sec-butyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl.

E is preferably $-OR^{29}$; $-SR^{29}$; $-NR^{25}R^{25}$; $-COR^{28}$; $-COOR^{27}$; $-CONR^{25}R^{25}$; or -CN; wherein R^{25}, R^{27}, R^{28} and R^{29} are independently of each other C_1-C_{18} alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, or C_6-C_{24} aryl, such as phenyl, naphthyl, or biphenyl. G is E, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl.

Among the above-mentioned groups Ar^2 the following groups are preferred:

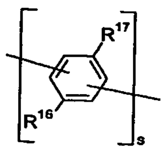


, wherein R^6, R^7, R^9 and R^{10} are defined as above and n1 and n2 are 1, 2, or 3.

The polymer of the present invention comprise the repeating unit of the formula I in an amount of from 0.5 mol% to 100 mol%, especially in an amount of from 20 mol% to 60 mol%, wherein the sum of all repeating units (monomers) is 100 mol%. Accordingly, the polymers of the present invention can comprise besides the repeating unit of the formula I additional

repeating units in an amount of up to 99.5 mol%, especially in an amount of from 80 mol% to 40 mol%.

Suitable additional repeating units T are selected from the group consisting of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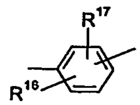
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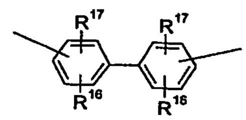
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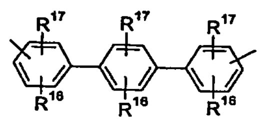
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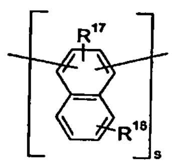
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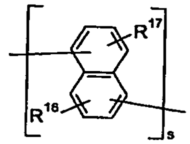
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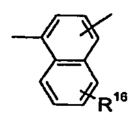
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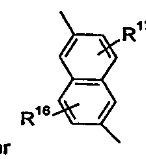
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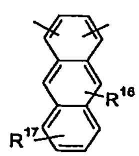
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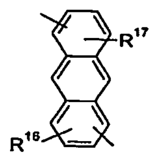
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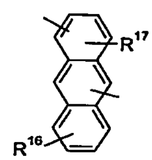
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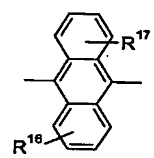
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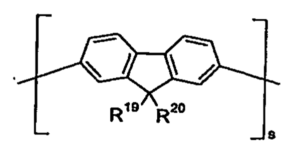
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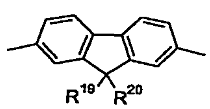
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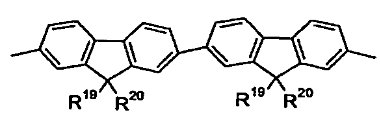
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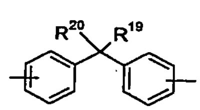
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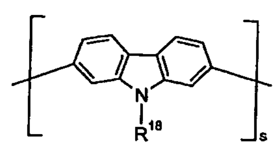
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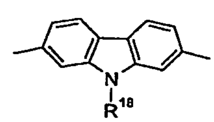
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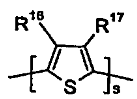
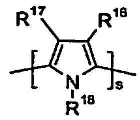
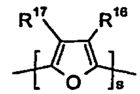
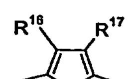
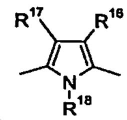
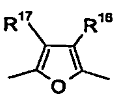
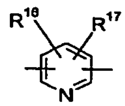
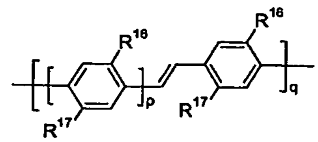
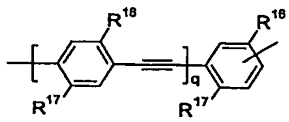
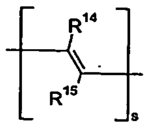
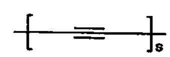
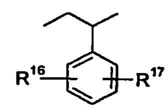
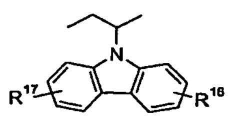
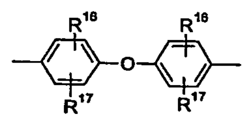
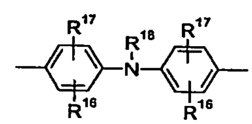
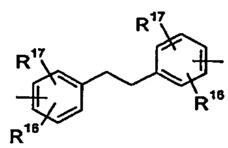
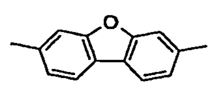
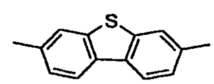
, , or , especially , , or

, , , or

, , , ,

, , ,

, , or , wherein

p is an integer from 1 to 10, especially 1, 2 or 3,

q is an integer from 1 to 10, especially 1, 2 or 3,

s is an integer from 1 to 10, especially 1, 2 or 3,

R^{14} and R^{15} are independently of each other H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, or C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G,

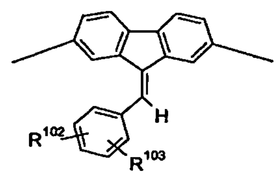
R^{16} and R^{17} are independently of each other H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or -CO-R^{28},

R^{18} is H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl, or C_1-C_{18}alkyl which is interrupted by –O–;

R^{19} and R^{20} are independently of each other C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl,

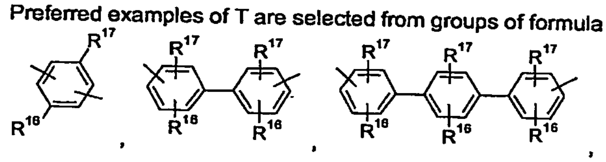
C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, or C_7-C_{25}aralkyl,
R^{19} and R^{20} together form a group of formula $=CR^{100}R^{101}$, wherein
R^{100} and R^{101} are independently of each other H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G, or
R^{19} and R^{20} form a ring, especially a five- or six-membered ring, and
D and E are as defined above.

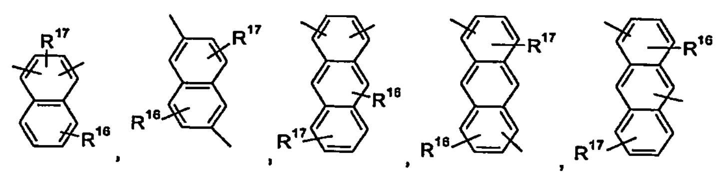
If R^{19} and R^{20} together form a group of formula $=CR^{100}R^{101}$, T is preferably a group of formula

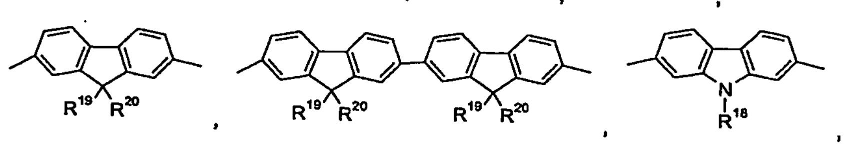


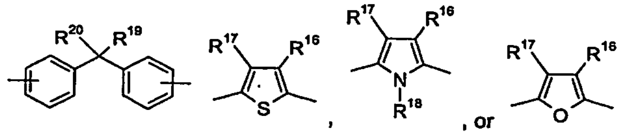
, wherein R^{102} and R^{103} are independently of each other C_1-C_{18}alkyl, C_1-C_{18}alkoxy, C_6-C_{10}aryl, C_6-C_{10}aryloxy, or di(C_1-C_{18}alkyl)amino, wherein the aryl or aryloxy groups optionally can be substituted by C_1-C_8alkyl (cf. US-B-6,512,083).

Preferred examples of T are selected from groups of formula









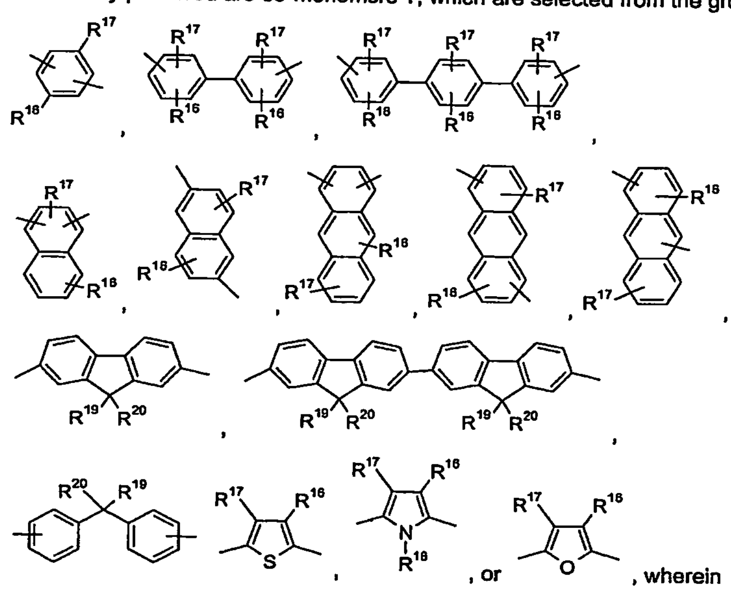
, wherein

R^{16} and R^{17} are independently of each other H, C_1-C_{18} alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, such as $-CH_2OCH_3$, $-CH_2OCH_2CH_3$, $-CH_2OCH_2CH_2OCH_3$, or $-CH_2OCH_2CH_2OCH_2CH_3$, C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl, C_6-C_{24}aryl which is substituted by G, such as $-C_6H_4OCH_3$, $-C_6H_4OCH_2CH_3$, $-C_6H_3(OCH_3)_2$, or $-C_6H_3(OCH_2CH_3)_2$, $-C_6H_4CH_3$, $-C_6H_3(CH_3)_2$, $-C_6H_2(CH_3)_3$, or $-C_6H_4tBu$,

R^{18} is H, C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, n-heptyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl, and

R^{19} and R^{20} are independently H, C_1-C_{18}alkyl, such as n-butyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, such as $-CH_2(OCH_2CH_2)_wOCH_3$, w = 1, 2, 3, or 4, C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl, C_6-C_{24}aryl which is substituted by G, such as $-C_6H_4OCH_3$, $-C_6H_4OCH_2CH_3$, $-C_6H_3(OCH_3)_2$, $-C_6H_3(OCH_2CH_3)_2$, $-C_6H_4CH_3$, $-C_6H_3(CH_3)_2$, $-C_6H_2(CH_3)_3$, or $-C_6H_4tBu$, or R^9 and R^{10} together form a 4 to 8 membered ring, especially a 5 or 6 membered ring, such as cyclohexyl, or cyclopentyl.

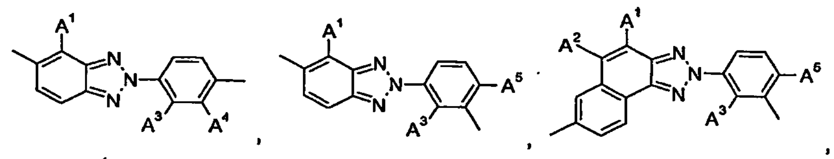
Particularly preferred are co-monomers T, which are selected from the group consisting of

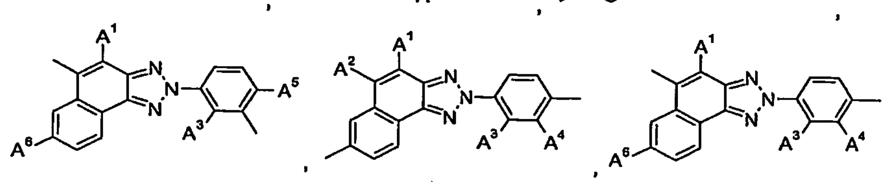


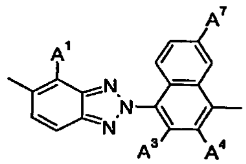
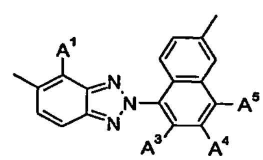
, wherein

R^{16} and R^{17} are independently of each other C_1-C_{18}alkyl, especially C_4-C_{12}alkyl, which can be interrupted by one or two oxygen atoms,
R^{18} is C_1-C_{18}alkyl, and
R^{19} and R^{20} are independently of each other C_1-C_{18}alkyl, especially C_4-C_{12}alkyl, which can be interrupted by one or two oxygen atoms, or
R^{19} and R^{20} form a five or six membered carbocyclic ring, which optionally can be substituted by C_1-C_4alkyl.

Especially preferred are polymers, comprising a repeating unit of the formula



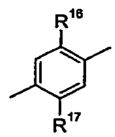
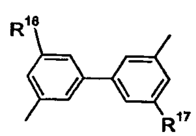
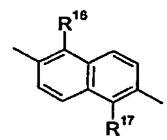


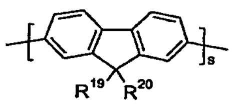
 and/or , and a co-monomer T in an amount of 0 to 99.5 mol%, especially in an amount of 40 to 80 mol%, wherein the sum of the repeating unit(s) and the co-monomer is 100 mol%, wherein
A^1 is hydrogen, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl,
A^2 is hydrogen, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl,
A^3 is hydrogen, or C_1-C_{18}alkoxy, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl,
A^4 is hydrogen, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl,
A^5 is hydrogen, C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl, di(C_1-

C_{18}alkyl)amino, or C_1-C_{18}alkoxy, such as methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, isobutoxy, sec-butoxy, t-butoxy, 2-methylbutoxy, n-pentoxy, isopentoxy, n-hexoxy, 2-ethylhexoxy, or n-heptoxy,

A^6 is hydrogen, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl,

A^7 is hydrogen, C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl, or C_1-C_{18}alkoxy, such as methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, isobutoxy, sec-butoxy, t-butoxy, 2-methylbutoxy, n-pentoxy, isopentoxy, n-hexoxy, 2-ethylhexoxy, or n-heptoxy, and

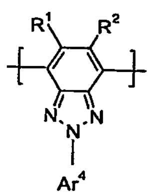
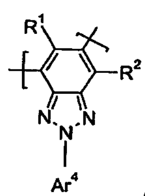
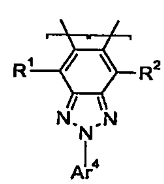
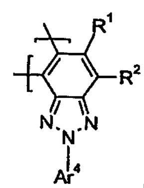
T is a group of formula  ,  ,  ,

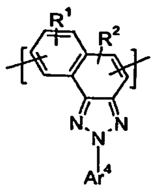
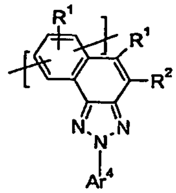
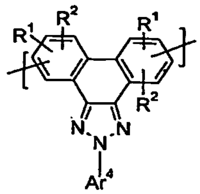
or  , wherein s is one or two,

R^{16} and R^{17} are independently of each other C_1-C_{18}alkyl, especially C_4-C_{12}alkyl, especially hexyl, heptyl, 2-ethylhexyl, and octyl, which can be interrupted by one or two oxygen atoms, C_1-C_{18}alkoxy, especially C_4-C_{12}alkoxy, especially hexyloxy, heptyloxy, 2-ethylhexyloxy, and octyloxy, which can be interrupted by one or two oxygen atoms,

and R^{19} and R^{20} are independently of each other C_1-C_{18}alkyl, especially C_4-C_{12}alkyl, especially hexyl, heptyl, 2-ethylhexyl, and octyl, which can be interrupted by one or two oxygen atoms.

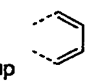
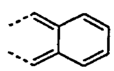
In another aspect, the polymers of the present invention comprise repeating units of formula II. Examples of repeating units of the formula II are

 (IIa), especially  (IIb),  (IIc),  (IId),

 (IIe),  (IIf), or  (IIg),

wherein Ar^4 is as defined above,

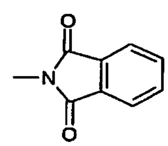
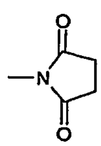
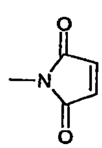
R^1 and R^2 are independently of each other H, halogen, SO_3^-, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_1-C_{18}perfluoroalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or -CO-R^{28},

or two substituents R^1 and R^2, which are adjacent to each other, are a group , or ,

D is -CO-; -COO-; -S-; -SO-; -SO_2-; -O-; -NR^{25}-; -$SiR^{30}R^{31}$-; -POR^{32}-; -CR^{23}=CR^{24}-; or -C≡C-; and

E is -OR^{29}; -SR^{29}; -$NR^{25}R^{26}$; -COR^{28}; -$COOR^{27}$; -$CONR^{25}R^{26}$; -CN; -$OCOOR^{27}$; or halogen; G is E, or C_1-C_{18}alkyl, wherein

R^{23}, R^{24}, R^{25} and R^{26} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-; or

R^{25} and R^{26} together form a five or six membered ring, in particular , , or ,

R^{27} and R^{28} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-,

R^{29} is H; C_6-C_{18}aryl; C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-,

R^{30} and R^{31} are independently of each other C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, and

R^{32} is C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl.

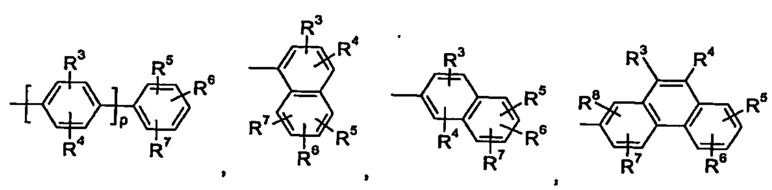
Repeating units of formula (IIe), (IIf), and (IIg) are most preferred.

Preferably, R^1 and R^2 are independently of each other H, C_1-C_{18}alkyl, such as as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, or sec-butyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl.

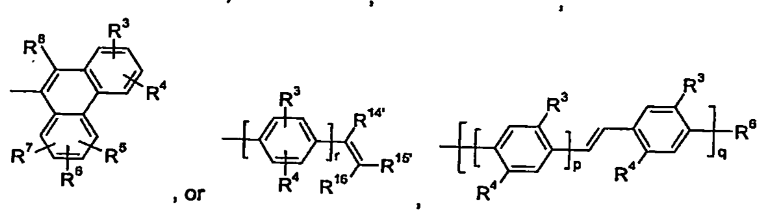
D is preferably -CO-, -COO-, -S-, -SO-, $-SO_2-$, -O-, $-NR^{25}-$, wherein R^{25} is C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, or sec-butyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl.

E is preferably $-OR^{29}$; $-SR^{29}$; $-NR^{25}R^{25}$; $-COR^{28}$; $-COOR^{27}$; $-CONR^{25}R^{25}$; or -CN; wherein R^{25}, R^{27}, R^{28} and R^{29} are independently of each other C_1-C_{18} alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, or C_6-C_{24} aryl, such as phenyl, naphthyl, or biphenyl. G is E, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl.

Ar^4 is preferably a group of formula



, or



, wherein

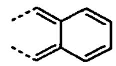
p is an integer from 1 to 10, especially 1, 2 or 3,

q is an integer from 1 to 10, especially 1, 2 or 3,

r is an integer of 0 to 10, in particular 0, 1, 2 or 3,

R^3 to R^8 are independently of each other H, halogen, SO_3^-, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or -CO-R^{28}, or

two substituents R^3 to R^8, which are adjacent to each other, are a group , or

, and

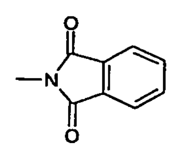
$R^{14'}$ and $R^{15'}$ are independently of each other H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G,

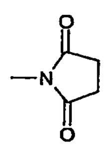
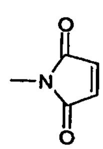
R^{16} is C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, which optionally can be substituted, wherein

D is -CO-; -COO-; -S-; -SO-; -SO_2-; -O-; -NR^{25}-; -$SiR^{30}R^{31}$-; -POR^{32}-; -CR^{23}=CR^{24}-; or -C≡C-; and

E is -OR^{29}; -SR^{29}; -$NR^{25}R^{26}$; -COR^{28}; -$COOR^{27}$; -$CONR^{25}R^{26}$; -CN; -$OCOOR^{27}$; or halogen; G is E, or C_1-C_{18}alkyl, wherein

R^{23}, R^{24}, R^{25} and R^{26} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-; or

R^{25} and R^{26} together form a five or six membered ring, in particular ,

, or ,

R^{27} and R^{28} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-,

R^{29} is H; C_6-C_{18}aryl; C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-,

R^{30} and R^{31} are independently of each other C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, and
R^{32} is C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl.

Preferably, R^3, R^4, R^5, R^6, R^7 and R^8 are independently of each other H, C_1-C_{18} alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, such as $-CH_2OCH_3$, $-CH_2OCH_2CH_3$, $-CH_2OCH_2CH_2OCH_3$, or $-CH_2OCH_2CH_2OCH_2CH_3$, C_6-C_{24}aryl, such as phenyl, naphthyl, or biphenyl, C_6-C_{24}aryl which is substituted by G, such as $-C_6H_4OCH_3$, $-C_6H_4OCH_2CH_3$, $-C_6H_3(OCH_3)_2$, or $-C_6H_3(OCH_2CH_3)_2$, $-C_6H_4CH_3$, $-C_6H_3(CH_3)_2$, $-C_6H_2(CH_3)_3$, or $-C_6H_4tBu$.

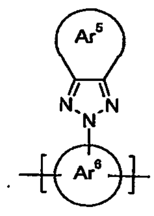
Preferably, $R^{14'}$ and $R^{15'}$ are independently of each other H, C_1-C_{18}alkyl, such as as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, and sec-butyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, and biphenyl.

R^{16} is preferably H, C_1-C_{18}alkyl, such as as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, and sec-butyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, and biphenyl.

D is preferably -CO-, -COO-, -S-, -SO-, $-SO_2-$, -O-, $-NR^{25}-$, wherein R^{25} is C_1-C_{18} alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, hexyl, octyl, and 2-ethyl-hexyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, and biphenyl.

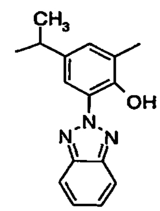
E is preferably $-OR^{29}$, $-SR^{29}$, $-NR^{25}R^{25}$, $-COR^{28}$, $-COOR^{27}$, $-CONR^{25}R^{25}$, or -CN, wherein R^{25}, R^{27}, R^{28} and R^{29} are independently of each other C_1-C_{18} alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, 2-ethyl-hexyl, or C_6-C_{24} aryl, such as phenyl, naphthyl, and biphenyl. G is E, or C_1-C_{18} alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, 2-ethyl-hexyl.

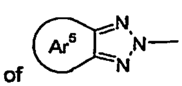
Another aspect of the present invention, is directed to polymers, comprising repeating units of the formula

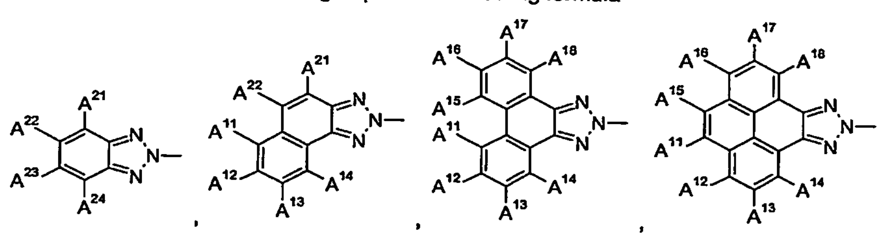


(III), wherein

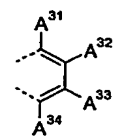
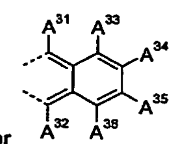
Ar^5 and Ar^6 are independently of each other an aryl group, or a heteroaryl group, which can optionally be substituted, especially a C_6-C_{30}aryl group, or a C_2-C_{26}heteroaryl group, which can optionally be substituted.

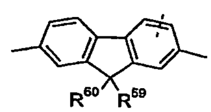
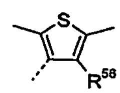
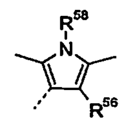
The repeating unit of formula III is not a repeating unit of formula  , especially Ar^6 is not a phenyl group substituted by a hydroxy group in ortho position to the bonding to the benzotriazole unit.

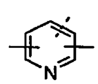
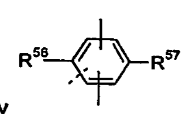
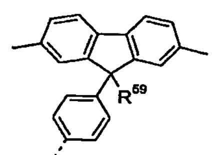
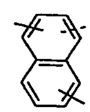
Examples of  are groups of the following formula

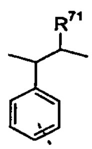


wherein A^{21}, A^{22}, A^{23}, A^{24}, A^{11}, A^{12}, A^{13}, A^{14}, A^{15}, A^{16}, A^{17} and A^{18} are independently of each other H, halogen, SO_3^-, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_1-C_{18}perfluoroalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or -CO-R^{28}, wherein E, D, G and R^{28} are defined as above, or two groups A^{11}, A^{12}, A^{13}, A^{14}, A^{15}, A^{16}, A^{17}

and A^{18}, which are neighbouring to each other, are a group  , or  ,
wherein A^{31}, A^{32}, A^{33}, A^{34}, A^{35}, A^{36} and A^{37} are independently of each other H, halogen, SO_3^-, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_1-C_{18}perfluoroalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or -CO-R^{28}.

Examples of Ar^6 are groups of formula  ;  ;  ; or

 ; especially  ;  ;  ;  , or



; wherein the dotted line represent the bond to the benzotriazole ring;

R^{56} and R^{57} are independently of each other H; C_1-C_{18}alkyl; C_1-C_{18}alkyl which is substituted by E and/or interrupted by D; C_6-C_{24}aryl; C_6-C_{24}aryl which is substituted by G; C_2-C_{20}heteroaryl; C_2-C_{20}heteroaryl which is substituted by G; C_2-C_{18}alkenyl; C_2-C_{18}alkynyl; C_1-C_{18}alkoxy; C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D; or C_7-C_{25}aralkyl;

R^{58} is H; C_1-C_{18}alkyl; C_1-C_{18}alkyl which is substituted by E and/or interrupted by D; C_6-C_{24}aryl; or C_7-C_{25}aralkyl;

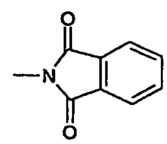
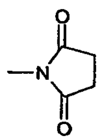
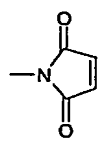
R^{59} and R^{60} are independently of each other H; C_1-C_{18} alkyl; C_1-C_{18}alkyl which is substituted by E and/or interrupted by D; C_6-C_{24}aryl; C_6-C_{24}aryl which is substituted by G; C_2-C_{20}heteroaryl; C_2-C_{20}heteroaryl which is substituted by G; C_2-C_{18}alkenyl; C_2-C_{18}alkynyl; C_1-C_{18}alkoxy; C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D; or C_7-C_{25}aralkyl;

R^{71} is H, C_1-C_{18}alkyl, -C≡N, -CONR^{25}R^{26} or -COOR^{27},

D is -CO-; -COO-; -OCOO-; -S-; -SO-; -SO_2-; -O-; -NR^{25}-; -SiR^{30}R^{31}-; -POR^{32}-; -CR^{23}=CR^{24}-; or -C≡C-; and

E is $-OR^{29}$; $-SR^{29}$; $-NR^{25}R^{26}$; $-COR^{28}$; $-COOR^{27}$; $-CONR^{25}R^{26}$; -CN; $-OCOOR^{27}$; or halogen; G is E, or C_1-C_{18}alkyl, wherein

R^{23}; R^{24}; R^{25} and R^{26} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl; C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-; or

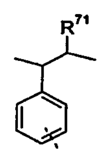
R^{25} and R^{26} together form a five or six membered ring, in particular , , or ,

R^{27} and R^{28} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-, and

R^{29} is H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-,

R^{30} and R^{31} are independently of each other C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, and

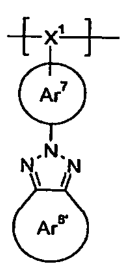
R^{32} is C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl.

Most preferred, Ar^8 is a group of the formula , wherein the dotted line represent the bond to the benzotriazole ring and R^{71} is H, alkyl, -C≡N, or $-COOR^{27}$, wherein R^{27} is H, or C_1-C_{18}alkyl, which optionally can be interrupted by one or more oxygen atoms, especially C_4-C_{12}alkyl, which can be interrupted by one or two oxygen atoms.

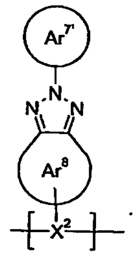
The polymer of the present invention comprise the repeating unit of the formula II and/or III in an amount of from 0.5 mol% to 100 mol%, especially in an amount of from 20 mol% to 80 mol%, wherein the sum of all repeating units (monomers) is 100 mol%. Accordingly, the polymers of the present invention can comprise besides the repeating unit of the formula II and/or III additional repeating units in an amount of up to 99.5 mol%, especially in an amount

of from 80 mol% to 40 mol%. Suitable additional repeating units are the repeating units T described for the polymers comprising repeating units of the formula I.

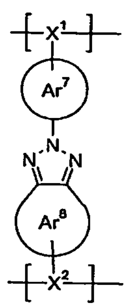
As stated above among the repeating units of the formula IV, repeating units of the formula



(IVa), and



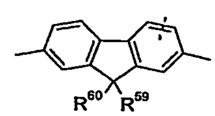
(IVb), are preferred against repeating units of the formula



(IVc), wherein

Ar^7, $Ar^{7'}$, Ar^8 and $Ar^{8'}$ are independently of each other a C_6-C_{30}aryl group, or a C_2-C_{26}heteroaryl group, which can optionally be substituted,

X^1 and X^2 are independently of each other a group of the formula



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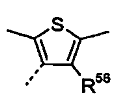

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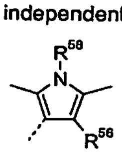
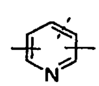
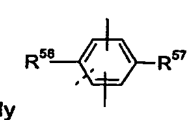


, or



; especially



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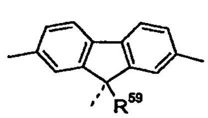
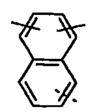
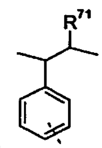
 ,  ,  or  , wherein the dotted line represent the bond to the benzotriazole unit,

R^{56} and R^{57} are independently of each other H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, or C_7-C_{25}aralkyl,

R^{58} is H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, or C_7-C_{25}aralkyl,

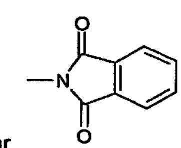
R^{59} and R^{60} are independently of each other H, C_1-C_{18} alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, or C_7-C_{25}aralkyl, or R^{59} and R^{60} form a ring, especially a five- or six-membered ring,

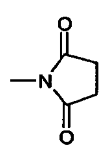
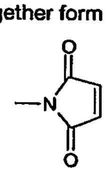
R^{71} is H, C_1-C_{18}alkyl, -C≡N, -CONR^{25}R^{26} or -COOR^{27},

D is -CO-; -COO-; -OCOO-; -S-; -SO-; -SO_2-; -O-; -NR^{25}-; -SiR^{30}R^{31}-; -POR^{32}-; -CR^{23}=CR^{24}-; or -C≡C-; and

E is -OR^{29}; -SR^{29}; -NR^{25}R^{26}; -COR^{28}; -COOR^{27}; -CONR^{25}R^{26}; -CN; -OCOOR^{27}; or halogen; G is E, or C_1-C_{18}alkyl, wherein

R^{23}, R^{24}, R^{25} and R^{26} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-; or

R^{25} and R^{26} together form a five or six membered ring, in particular  ,

 , or  ,

R^{27} and R^{28} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or $_1$-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-, and

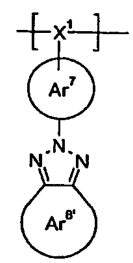
R^{29} is H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O–,
R^{30} and R^{31} are independently of each other C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl, and
R^{32} is C_1-C_{18}alkyl, C_6-C_{18}aryl, or C_6-C_{18}aryl, which is substituted by C_1-C_{18}alkyl.

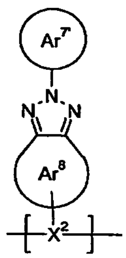
Preferably, R^{56} and R^{57} are independently of each other H, C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, and n-heptyl, C_1-C_{18}alkyl, which is substituted by E and/or interrupted by D, such as $-CH_2OCH_3$, $-CH_2OCH_2CH_3$, $-CH_2OCH_2CH_2OCH_3$, and $-CH_2OCH_2CH_2OCH_2CH_3$, C_6-C_{24}aryl, such as phenyl, naphthyl, and biphenyl, or C_6-C_{24}aryl, which is substituted by g, such as $-C_6H_4OCH_3$, $-C_6H_4OCH_2CH_3$, $-C_6H_3(OCH_3)_2$, $-C_6H_3(OCH_2CH_3)_2$, $-C_6H_4CH_3$, $-C_6H_3(CH_3)_2$, $-C_6H_2(CH_3)_3$, and $-C_6H_4tBu$.

R^{58} is preferably H, C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, and n-heptyl, or C_6-C_{24}aryl, such as phenyl, naphthyl, and biphenyl.

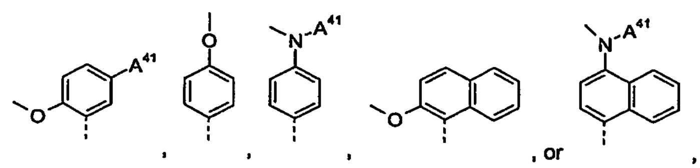
Preferably, R^{59} and R^{60} are independently of each other H, C_1-C_{18}alkyl, such as n-butyl, sec-butyl, hexyl, octyl, and 2-ethyl-hexyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, such as $-CH_2(OCH_2CH_2)_wOCH_3$, w=1, 2, 3, or 4, C_6-C_{24}aryl, such as phenyl, naphthyl, and biphenyl, C_6-C_{24} aryl which is substituted by G, such as $-C_6H_4OCH_3$, $-C_6H_4OCH_2CH_3$, $-C_6H_3(OCH_3)_2$, $-C_6H_3(OCH_2CH_3)_2$, $-C_6H_4CH_3$, $-C_6H_3(CH_3)_2$, $-C_6H_2(CH_3)_3$, and $-C_6H_4tBu$, or R^{59} and R^{60} together form a 4 to 8 membered ring, preferably a 5 or 6 membered ring, such as cyclohexyl, and cyclopentyl.

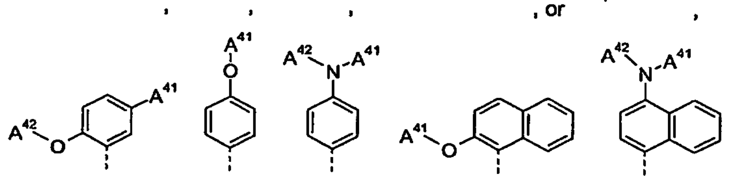
R^{71} is preferably H, $-CONR^{25}R^{25}$ or -CN, wherein R^{25} is H, C_1-C_{18} alkyl, or C_6-C_{24} aryl, such as phenyl, naphthyl, and biphenyl.

Most preferred are polymers, comprising a repeating unit of the formula  (IVa),

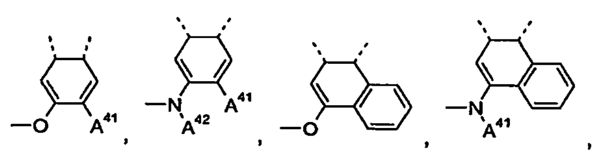


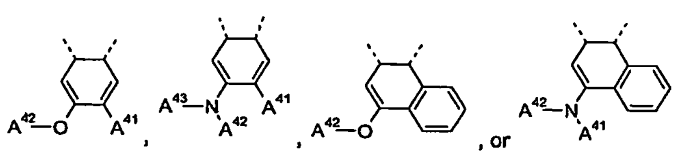
and/or (IVb), and a repeating unit T in an amount of 0 to 99.5 mol%, especially in an amount of 40 to 80 mol%, wherein the sum of the repeating unit(s) and the comonomer is 100 mol%, wherein

Ar^7 is 

$Ar^{7'}$ is 

wherein the dotted line is the bond to the nitrogen atom of the benzotriazole unit,

Ar^8 is 

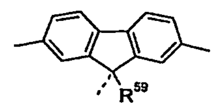
$Ar^{8'}$ is 

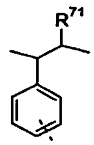
wherein the dotted lines are the bonds to the nitrogen atoms of the benzotriazole unit,

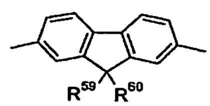
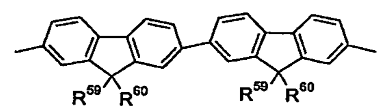
A^{41} is hydrogen, C_1-C_{18}alkoxy, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl,

A^{42} is hydrogen, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl,

A^{43} is hydrogen, or C_1-C_{18}alkoxy, or C_1-C_{18}alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl,

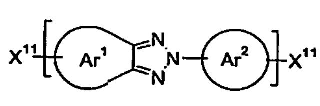
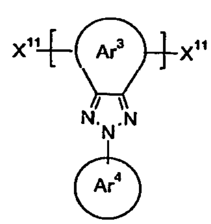
X^1 and X^2 are independently of each other a group of the formula  , or

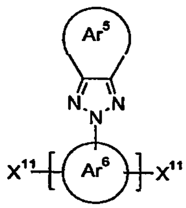
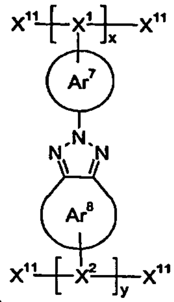
 , wherein the dotted line represent the bond to the benzotriazole unit,
R^{71} is H, C_1-C_{18}alkyl, -C≡N, or -COOR^{27}, wherein
R^{27} is H; or C_1-C_{18}alkyl, which can be interrupted by one or more oxygen atoms, especially C_4-C_{12}alkyl, which can be interrupted by one or two oxygen atoms, and

T is a group of formula  , or  ,
wherein R^{59} and R^{60} are independently of each other C_1-C_{18}alkyl, especially C_4-C_{12}alkyl, which can be interrupted by one or two oxygen atoms.

The polymers of this invention preferably have a weight average molecular weight of 50,000 Daltons or greater, more preferably 100,000 Daltons or greater, and most preferably 150,000 Daltons or greater; preferably 1,000,000 Daltons or less, more preferably 500,000 Daltons or less and most preferably 250,000 Daltons or less. Molecular weights are determined according to gel permeation chromatography using polystyrene standards.

A further embodiment of the present invention is represented by the monomers of the formula

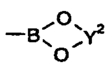
 (V),  (VI), or

 (VII), or  (VIII), wherein

x and y are 0 or 1,

Ar^1, Ar^2, Ar^3, Ar^4, Ar^5, and Ar^6 are independently of each other an aryl group, or a heteroaryl group, which optionally can be substituted, especially a C_6-C_{30}aryl group, or a C_2-C_{26}heteroaryl group, which can optionally be substituted, and

X^{11} is independently in each occurrence a halogen atom, or $-B(OH)_2$, $-B(OY^1)_2$ or

, wherein Y^1 is independently in each occurrence a C_1-C_{10}alkyl group and Y^2 is independently in each occurrence a C_2-C_{10}alkylene group, such as $-CY^3Y^4$-CY^5Y^6-, or $-CY^7Y^8$-CY^9Y^{10}- $CY^{11}Y^{12}$-, wherein Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11} and Y^{12} are independently of each other hydrogen, or a C_1-C_{10}alkyl group, especially $-C(CH_3)_2C(CH_3)_2$-, or $-C(CH_3)_2CH_2C(CH_3)_2$-, which are starting materials in the preparation of the polymers of formula I to IV.

Halogen is fluorine, chlorine, bromine and iodine.

C_1-C_{18}alkyl is a branched or unbranched radical such as for example methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, or octadecyl.

C_1-C_{18}perfluoroalkyl is a branched or unbranched radical such as for example $-CF_3$, $-CF_2CF_3$, $-CF_2CF_2CF_3$, $-CF(CF_3)_2$, $-(CF_2)_3CF_3$, and $-C(CF_3)_3$.

C_1-C_{18}alkoxy radicals are straight-chain or branched alkoxy radicals, e.g. methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, amyloxy, isoamyloxy or tert-amyloxy, heptyloxy, octyloxy, isooctyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy and octadecyloxy.

C_2-C_{18}alkenyl radicals are straight-chain or branched alkenyl radicals, such as e.g. vinyl, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-dodec-2-enyl or n-octadec-4-enyl.

C_{2-24}alkynyl is straight-chain or branched and preferably C_{2-8}alkynyl, which may be unsubstituted or substituted, such as, for example, ethynyl, 1-propyn-3-yl, 1-butyn-4-yl, 1-pentyn-5-yl, 2-methyl-3-butyn-2-yl, 1,4-pentadiyn-3-yl, 1,3-pentadiyn-5-yl, 1-hexyn-6-yl, cis-3-methyl-2-penten-4-yn-1-yl, trans-3-methyl-2-penten-4-yn-1-yl, 1,3-hexadiyn-5-yl, 1-octyn-8-yl, 1-nonyn-9-yl, 1-decyn-10-yl, or 1-tetracosyn-24-yl.

C_4-C_{18}cycloalkyl is preferably C_5-C_{12}cycloalkyl, such as, for example, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclododecyl. Cyclohexyl and cyclopentyl are most preferred.

C_2-C_{18}alkenyl is for example vinyl, allyl, butenyl, pentenyl, hexenyl, heptenyl, or octenyl.

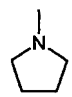
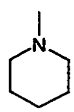
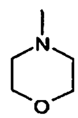
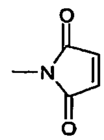
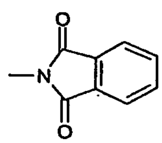
Aryl is usually C_6-C_{30}aryl, preferably C_6-C_{24}aryl, which optionally can be substituted, such as, for example, phenyl, 4-methylphenyl, 4-methoxyphenyl, naphthyl, biphenylyl, 2-fluorenyl, phenanthryl, anthryl, tetracyl, pentacyl, hexacyl, terphenylyl or quadphenylyl.

C_7-C_{24}aralkyl radicals are preferably C_7-C_{15}aralkyl radicals, which may be substituted, such as, for example, benzyl, 2-benzyl-2-propyl, β-phenethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, ω-phenyl-octyl, ω-phenyl-dodecyl or 3-methyl-5-(1',1',3',3'-tetramethyl-butyl)-benzyl.

C_2-C_{26}heteroaryl is a ring with five to seven ring atoms or a condensed rig system, wherein nitrogen, oxygen or sulfur are the possible hetero atoms, and is typically an unsaturated heterocyclic radical with five to 30 atoms having at least six conjugated π-electrons such as thienyl, benzo[b]thienyl, dibenzo[b,d]thienyl, thianthrenyl, furyl, furfuryl, 2H-pyranyl, benzofuranyl, isobenzofuranyl, dibenzofuranyl, phenoxythienyl, pyrrolyl, imidazolyl, pyrazolyl, pyridyl, bipyridyl, triazinyl, pyrimidinyl, pyrazinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, chinolyl, isochinolyl, phthalazinyl, naphthyridinyl, chinoxalinyl,

chinazolinyl, cinnolinyl, pteridinyl, carbazolyl, carbolinyl, benzotriazolyl, benzoxazolyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl or phenoxazinyl, which can be unsubstituted or substituted.

Examples of a five or six membered ring formed by R^6 and R^7 and R^{56} and R^{57}, respectively are heterocycloalkanes or heterocycloalkenes having from 3 to 5 carbon atoms which can have one additional hetero atom selected from nitrogen, oxygen and sulfur, for example

, , , or , which can be part of a bicyclic system, for example  or .

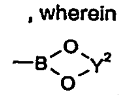
Possible substituents of the above-mentioned groups are C_1-C_8alkyl, a hydroxyl group, a mercapto group, C_1-C_8alkoxy, C_1-C_8alkylthio, halogen, halo-C_1-C_8alkyl, a cyano group, an aldehyde group, a ketone group, a carboxyl group, an ester group, a carbamoyl group, an amino group, a nitro group or a silyl group.

The term "haloalkyl" means groups given by partially or wholly substituting the above-mentioned alkyl group with halogen, such as trifluoromethyl etc. The "aldehyde group, ketone group, ester group, carbamoyl group and amino group" include those substituted by an C_1-C_{18}alkyl group, a C_4-C_{18}cycloalkyl group, an C_6-C_{30}aryl group, an C_7-C_{24}aralkyl group or a heterocyclic group, wherein the alkyl group, the cycloalkyl group, the aryl group, the aralkyl group and the heterocyclic group may be unsubstituted or substituted. The term "silyl group" means a group of formula $-SiR^{105}R^{106}R^{107}$, wherein R^{105}, R^{106} and R^{107} are independently of each other a C_1-C_8alkyl group, in particular a C_1-C_4 alkyl group, a C_6-C_{24}aryl group or a C_7-C_{12}aralkylgroup, such as a trimethylsilyl group.

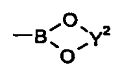
If a substituent, such as, for example R^6, R^7, R^{56} and R^{57}, occurs more than one time in a group, it can be different in each occurrence.

As described above, the aforementioned radicals may be substituted by E and/or, if desired, interrupted by D. Interruptions are of course possible only in the case of radicals containing at least 2 carbon atoms connected to one another by single bonds; C_6-C_{18}aryl is not interrupted; interrupted arylalkyl or alkylaryl contains the unit D in the alkyl moiety. C_1-C_{18}alkyl substituted by one or more E and/or interrupted by one or more units D is, for example, $(CH_2CH_2O)_n$-R^x, where n is a number from the range 1-9 and R^x is H or C_1-C_{10}alkyl or C_2-C_{10}alkanoyl (e.g. CO-$CH(C_2H_5)C_4H_9$), CH_2-$CH(OR^{y'})$-CH_2-O-R^y, where R^y is C_1-C_{18}alkyl, C_5-C_{12}cycloalkyl, phenyl, C_7-C_{15}phenylalkyl, and $R^{y'}$ embraces the same definitions as R^y or is H; C_1-C_8alkylene-COO-R^z, e.g. CH_2COOR^z, $CH(CH_3)COOR^z$, $C(CH_3)_2COOR^z$, where R^z is H, C_1-C_{18}alkyl, $(CH_2CH_2O)_{1-9}$-R^x, and R^x embraces the definitions indicated above; CH_2CH_2-O-CO-CH=CH_2; $CH_2CH(OH)CH_2$-O-CO-$C(CH_3)$=CH_2.

The polymers containing groups of formulas (I), (II), (III) and (IV) may be prepared by any suitable process, but are preferably prepared by the processes described below. The condensation reaction of an aromatic boronate and a bromide, commonly referred to as the "Suzuki reaction", is tolerant of the presence of a variety of organic functional groups and as reported by N. Miyaua and A. Suzuki in Chemical Reviews, Vol. 95, pp. 457-2483 (1995). This reaction can be applied to preparing high molecular weight polymers and copolymers.

To prepare polymers corresponding to formula (I), (II), (III) or (IV), a dibromide corresponding to formula V, VI, VII, or VIII, or a mixture thereof is reacted with an equimolar amount of diboronic acid or diboronate corresponding to formula V, VI, VII, or VIII, or a mixture thereof, preferably a co-monomer $X^{11}\!-\!\left[T\right]\!-\!X^{11}$, wherein X^{11} is independently in each occurrence a halogen atom, or -$B(OH)_2$, -$B(OY^1)_2$ or , wherein Y^1 is independently in each occurrence a C_1-C_{10}alkyl group and Y^2 is independently in each occurrence a C_2-C_{10}alkylene group, such as $-CY^3Y^4$-CY^5Y^6-, or $-CY^7Y^8$-CY^9Y^{10}- $CY^{11}Y^{12}$-, wherein Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11} and Y^{12} are independently of each other hydrogen, or a C_1-C_{10}alkyl group, especially -$C(CH_3)_2C(CH_3)_2$-, or -$C(CH_3)_2CH_2C(CH_3)_2$-, under the catalytic action of Pd and triphenylphosphine. The reaction is typically conducted at about 70 °C to 120 °C in an aromatic hydrocarbon solvent such as toluene. Other solvents such as dimethylformamide and tetrahydrofuran can also be used alone, or in mixtures with an aromatic hydrocarbon. An aqueous base, preferably sodium carbonate or bicarbonate, is used as the HBr scavenger. Depending on the reactivities of the reactants, a polymerization reaction may take 2 to 100 hours. Organic bases, such as, for example, tetraalkylammonium hydroxide, and phase

transfer catalysts, such as, for exampleTBAB, can promote the activity of the boron (see, for example, Leadbeater & Marco; Angew. Chem. Int. Ed., 2003, 42, 1407 and references cited therein). Other variations of reaction conditions are given by T. I. Wallow and B. M. Novak in Journal of Organic Chemistry, Vol. 59, pp. 5034-5037 (1994); and M. Remmers, M. Schulze, and G. Wegner in Macromolecular Rapid Communications, Vol. 17, pp. 239-252 (1996).

An alternating copolymer results when a dibromide corresponding to formula V, VI, VII, or VIII is reacted with a diboronate corresponding to formula $X^{11}\!-\!\!\left[T\right]\!\!-\!X^{11}$, wherein X^{11} is independently in each occurrence $-B(OH)_2$, $-B(OY^1)_2$ or , wherein Y^1 is independently in each occurrence a C_1-C_{10}alkyl group and Y^2 is independently in each occurrence a C_2-C_{10}alkylene group, such as $-CY^3Y^4$-CY^5Y^6-, or $-CY^7Y^8$-CY^9Y^{10}- $CY^{11}Y^{12}$-, wherein Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11} and Y^{12} are independently of each other hydrogen, or a C_1-C_{10}alkyl group, especially $-C(CH_3)_2C(CH_3)_2$-, or $-C(CH_3)_2CH_2C(CH_3)_2$-. If desired, a monofunctional aryl halide or aryl boronate may be used as a chain-terminator in such reactions, which will result in the formation of a terminal aryl group.

Polymerization processes involving only dihalo-functional reactants may be carried out using nickel coupling reactions. One such coupling reaction was described by Colon et al. in Journal of Polymer Science, Part A, Polymer Chemistry Edition, Vol. 28, p. 367 (1990), and by Colon et al. in Journal of Organic Chemistry, Vol. 51, p. 2627 (1986). The reaction is typically conducted in a polar aprotic solvent (e.g., dimethylacetamide) with a catalytic amount of nickel salt, a substantial amount of triphenylphosphine and a large excess of zinc dust. A variant of this process is described by Ioyda et al. in Bulletin of the Chemical Society of Japan, Vol. 63, p. 80 (1990) wherein an organo-soluble iodide was used as an accelerator. Another nickel-coupling reaction was disclosed by Yamamoto in Progress in Polymer Science, Vol. 17, p. 1153 (1992) wherein a mixture of dihaloaromatic compounds were treated with an excess amount of nickel (1,5-cyclooctadiene) complex in an inert solvent. All nickel-coupling reactions when applied to reactant mixtures of two or more aromatic dihalides yield essentially random copolymers. Such polymerization reactions may be terminated by the addition of small amounts of water to the polymerization reaction mixture, which will replace the terminal halogen groups with hydrogen groups. Alternatively, a monofunctional aryl halide may be used as a chain-terminator in such reactions, which will result in the formation of a terminal aryl group.

In one embodiment, the polymers of the invention contain conjugated groups other than the benzotriazole groups described above. "Conjugated groups" refer to moieties containing double bonds, triple bonds and/or aromatic rings. Examples of such groups are the above mentioned co-monomers T. The incorporation of such groups into the polymer may be used to modify the light absorption, ionization potential, and/or electronic properties of the polymer. Such polymers may be prepared using the methods described above incorporating at least one conjugated compound different from the benzotriazole compounds described above. Such conjugated compounds, hereinafter referred to as "comonomers", have functional groups which permit them to copolymerize with the benzotriazole compounds. For example, dihalo-functional comonomers are preferably used in conjunction with dihalo-functional benzotriazole compounds in nickel-coupling polymerization reactions; dihalo-functional comonomers are preferably used in conjunction with benzotriazole-diboronic acids or benzotriazole-diboronates; and conjugated comonomers bearing diboronic acid or diboronate functionalities are preferably used in conjunction with dihalobenzotriazoles. For the purpose of preparing polymers of the invention, more than one diboronic acid/diboronate and more than one dibromide may be used in a Suzuki polymerization reaction so long as the total molar amount of diboronic acids/diboronates is essentially equivalent to the total amount of dibromides.

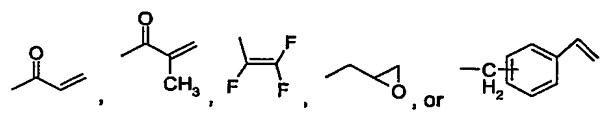
Nickel-coupling polymerizations yield essentially random copolymers comprising benzotriazole group-containing units and units derived from other co-monomers, while Suzuki polymerizations yield alternating copolymers.

It is possible to control the sequencing of the monomeric units in the resulting copolymer by controlling the order and composition of monomer feeds in the Suzuki reaction. For instance, a high molecular weight copolymer comprising mainly large blocks of benzotriazole homopolymers connected to short blocks of alternating benzotriazole co-monomer oligomers may be made by first introducing into the reaction reactants in the appropriate ratio to make the alternating benzotriazole-comonomer oligomers followed by the remainder of benzotriazole monomers so long as there is an overall balance of boronic and bromo groups.

Usually the polymers of the present invention comprise end moieties E^1, wherein E^1 is hydrogen or an aryl moiety which may optionally be substituted with a reactive group capable of undergoing chain extension or crosslinking, or a tri(C_1-C_{18})alkylsiloxy group. As used herein, a reactive group capable of undergoing chain extension or crosslinking refers to any group which is capable of reacting with another of the same group or another group so as to

form a link to prepare oligomers or polymers. Preferably, such reactive group is a hydroxy, glycidyl ether, acrylate ester, methacrylate ester, ethenyl, ethynyl, maleimide, nadimide, trifluorovinyl ether moiety or a cyclobutene moiety fused to the aromatic ring of E^1.

The polymers of the present invention, where E^1 are reactive groups as defined above, are capable of crosslinking to form solvent resistant, heat-resistant films at 100°C or more, more preferably at 150°C or more. Preferably, such crosslinking occurs at 350°C or less, more preferably 300°C or less and most preferably 250°C or less. The crosslinkable polymers of the invention are stable at 100°C or more and more preferably 150°C or more. "Stable" as used herein means that such polymers do not undergo crosslinking or polymerization reactions at or below the stated temperatures. If a crosslinkable material is desired, E^1 is preferably a vinylphenyl, an ethynylphenyl, or 4-(or 3-)benzocyclobutenyl radical. In another embodiment, E^1 is selected from a group of phenolic derivatives of the formula $-C_6H_4-O-Y$, wherein Y is

-H, -CN,  . If desired, the cross-linkable groups can be present in other parts of the polymer chain. For example, one of the substituents of the co-monomer T may be a crosslinkable group E^1.

The end-capping agent E^1-X (E^1 is as defined above and X is either Cl or Br) is incorporated into the polymers of the present invention under the condition in which the resulting polymers are substantially capped by the reactive group E^1. The reactions useful for this purpose are the nickel-coupling and Suzuki reactions described above. The average degree of polymerization is controlled by the mole ratio of monomers to end-capping agent.

Depending on the process of preparation the polymers of the present invention can be block copolymers, random copolymers, or alternating copolymers.

Another aspect of this invention is related to polymer blends containing 1 to 99 percent of at least one benzotriazole containing polymers of this invention. The remainder 1 percent to 99 percent of the blend is composed of one or more polymeric materials selected from among chain growth polymers such as polystyrene, polybutadiene, poly(methyl methacrylate), and poly(ethylene oxide); step-growth polymers such as phenoxy resins, polycarbonates, polyamides, polyesters, polyurethanes, and polyimides; and crosslinked polymers such as crosslinked epoxy resins, crosslinked phenolic resins, crosslinked acrylate resins, and

crosslinked urethane resins. Examples of these polymers may be found in Preparative Methods of Polymer Chemistry, W. R. Sorenson and T. W. Campbell, Second Edition, Interscience Publishers (1968). Also may be used in the blends are conjugated polymers such as poly(phenylene vinylene), substituted poly(phenylene vinylene)s, substituted polyphenylenes and polythiophenes. Examples of these conjugated polymers are given by Greenham and Friend in Solid State Physics, Vol. 49, pp. 1-149 (1995).

Another aspect of the invention is the films formed from the polymers of the invention. Such films can be used in polymeric light-emitting diodes. Preferably, such films are used as emitting layers. These polymers may also be used as protective coatings for electronic devices and as fluorescent coatings. The thickness of the coating or film is dependent upon the ultimate use. Generally, such thickness can be from 0.01 to 200 microns. In that embodiment wherein the coating is used as a fluorescent coating, the coating or film thickness is from 50 to 200 microns. In that embodiment where the coatings are used as electronic protective layers, the thickness of the coating can be from 5 to 20 microns. In that embodiment where the coatings are used in a polymeric light-emitting diode, the thickness of the layer formed is 0.01 to 2 microns. The polymers of the invention form good pinhole- and defect-free films. Such films can be prepared by means well known in the art including spin-coating, spray-coating, dip-coating and roller-coating. Such coatings are prepared by a process comprising applying a composition to a substrate and exposing the applied composition to conditions such that a film is formed. The conditions which form a film depend upon the application technique. In a preferred embodiment, the composition applied to the substrate comprises the benzotriazole polymers dissolved in a common organic solvent. Preferably, the solution contains from 0.1 to 10 weight percent of the polymers. This composition is applied to the appropriate substrate by the desired method and the solvent is allowed to evaporate. Residual solvent may be removed by vacuum and/or by heat. After removal of the solvent, the coating is then exposed to the necessary conditions to cure the film, if needed, to prepare a film having high solvent and heat resistance. The films are preferably substantially uniform in thickness and substantially free of pinholes. In another embodiment, the polymers may be partially cured. This is known as B-staging.

A further embodiment of the present invention is directed to an optical device or a component therefore, comprising a substrate and a polymer according to the present invention.

A device according to the present invention may be prepared in accordance with the disclosure of WO99/48160, the contents of which are incorporated by reference. Polymers

according to the present invention may be present in the device as the sole light emitting polymer or as a component in a blend further comprising hole and/or electron transporting polymers. Alternatively, the device may comprise distinct layers of a polymer of the present invention, a hole transporting polymer and/or an electron transporting polymer.

In one embodiment the optical device comprises an electroluminescent device, which comprises at least

(a) a reflective or transmissive anode

(b) a reflective or transmissive cathode

(c) an emissive layer comprising a polymer according to the present invention located between the electrodes

and optionally

(d) a charge injecting layer for injecting positive charge carriers, and

(e) a charge injecting layer for injecting negative charge carriers.

The layer (d) may be a positive charge carrier transport layer which is located between the light emissive layer (c) and an anode electrode layer, or may be an anode electrode layer. The layer (e) may be a negative charge carrier transport layer which is located between the light emissive layer (c) and a cathode electrode layer, or may be an cathode electrode layer. Optionally, an organic charge transport layer can be located between the light emissive layer (c) and one of the charge carrier injecting layers (d) and (e).

The EL device emits light below 520 nm, especially between 380 nm and 520 nm, very especially between 400 nm and 490 nm. The EL device emits blue light.

The EL device has a NTSC coordinate of between about (0.10, 0.02) and about (0.25, 0.25), especially a NTSC coordinate of about (0.14, 0.08).

It will be appreciated that the light emissive layer may be formed from a blend or mixture of materials including one or more polymers according to the present invention, and optionally further different polymers. The further different polymers may be so-called hole transport polymers (i.e. to improve the efficiency of hole transport to the light-emissive material) or electron-transport polymers (i.e. to improve the efficiency of electron transport to the light-emissive material). Preferably, the blend or mixture would comprise at least 0.1 % by weight of a polymer according to the present invention, preferably from 0.2 to 50%, more preferably from 0.5 to 30% by weight.

The light-emitting layer can be comprised of a single material, but more commonly consists of a host material, i.e. the polymers of the present invention, doped with a guest compound or compounds, where light emission comes primarily from the dopant and can be of any color. The dopant is usually chosen from highly fluorescent dyes, but phosphorescent compounds, e.g., transition metal complexes as described in WO 98/55561, WO 00/18851, WO 00/57676, and WO 00/70655 are also useful. The polymers of the present invention may also be employed as dopants within other host materials. Dopants are typically coated as 0.01 to 10% by weigh into the host material.

Host and emitting molecules known to be of use include, but are not limited to, those disclosed in U.S. Pat. Nos. 4,768,29; 5,141,671; 5,150,006; 5,151,629; 5,294,870; 5,405,709; 5,484,922; 5,593,788; 5,645,948; 5,683,823; 5,755,999; 5,928,802; 5,935,720; 5,935,721; and 6,020,078.

An organic EL device typically consists of an organic film sandwiched between an anode and a cathode such that when a forward bias is applied to the device, holes are injected into the organic film from the anode, and electrons are injected into the organic film from the cathode. The combination of a hole and an electron may give rise to an exciton, which may undergo radiative decay to the ground state by liberating a photon. In practice the anode is commonly a mixed oxide of tin and indium for its conductivity and transparency. The mixed oxide (ITO) is deposited on a transparent substrate such as glass or plastic so that the light emitted by the organic film may be observed. The organic film may be the composite of several individual layers each designed for a distinct function. Since holes are injected from the anode, the layer next to the anode needs to have the functionality of transporting holes. Similarly, the layer next to the cathode needs to have the functionality of transporting electrons. In many instances, the electron-(hole) transporting layer also acts as the emitting layer. In some instances one layer can perform the combined functions of hole and electron transport and light emission. The individual layers of the organic film may be all polymeric in nature or combinations of films of polymers and films of small molecules deposited by thermal evaporation. It is preferred that the total thickness of the organic film be less than 1000 nanometers (nm). It is more preferred that the total thickness be less than 500 nm. It is most preferred that the total thickness be less than 300 nm. It is preferred that the thickness of the active (light emitting) layer be less than 400 nanometers (nm). It is more preferred that the thickness is in the range of from 40 to 160 nm.

The ITO-glass which serves as the substrate and the anode may be used for coating after the usual cleaning with detergent, organic solvents and UV-ozone treatment. It may also be first coated with a thin layer of a conducting substance to facilitate hole injection. Such substances include copper phthalocyanine, polyaniline and poly(3,4-ethylenedioxy-thiophene) (PEDOT); the last two in their conductive forms by doping with a strong organic acid, e.g., poly(styrenesulfonic acid). It is preferred that the thickness of this layer be 200 nm or less; it is more preferred that the thickness be 100 nm or less.

In the cases where a hole-transporting layer is used, the polymeric arylamines described in U.S. Pat. No. 5,728,801, may be used. Other known hole-conducting polymers, such as polyvinylcarbazole, may also be used. The resistance of this layer to erosion by the solution of the polymer film which is to be applied next is obviously critical to the successful fabrication of multi-layer devices. The thickness of this layer may be 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less.

In the case where an electron-transporting layer is used, it may be applied either by thermal evaporation of low molecular weight materials or by solution coating of a polymer with a solvent that would not cause significant damage to the underlying film.

Examples of low molecular weight materials include the metal complexes of 8-hydroxyquinoline (as described by Burrows et al. in Applied Physics Letters, Vol. 64, pp. 2718-2720 (1994)), metallic complexes of 10-hydroxybenzo(h)quinoline (as described by Hamada et al. in Chemistry Letters, pp. 906-906 (1993)), 1,3,4-oxadiazoles (as described by Hamada et al. in Optoelectronics-Devices and Technologies, Vol. 7, pp. 83-93 (1992)), 1,3,4-triazoles (as described by Kido et al. in Chemistry Letters, pp. 47-48 (1996)), and dicarboximides of perylene (as described by Yoshida et al. in Applied Physics Letters, Vol. 69, pp. 734-736 (1996)). Further examples of low molecular weight materials are disclosed in the European patent application no. 03100972.3 , the content of which is incorporated herein by reference.

Polymeric electron-transporting materials are exemplified by 1,3,4-oxadiazole-containing polymers (as described by Li et al. in Journal of Chemical Society, pp. 2211-2212 (1995), by Yang and Pei in Journal of Applied Physics, Vol 77, pp. 4807-4809 (1995)), 1,3,4-triazole-containing polymers (as described by Strukelj et al. in Science, Vol. 267, pp. 1969-1972 (1995)), quinoxaline-containing polymers (as described by Yamamoto et al. in Japan Journal of Applied Physics, Vol. 33, pp. L250-L253 (1994), O'Brien et al. in Synthetic Metals, Vol. 76,

pp. 105-108 (1996)), and cyano-PPV (as described by Weaver et al. in Thin Solid Films, Vol. 273, pp. 39-47 (1996)). The thickness of this layer may be 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less.

The cathode may be deposited either by thermal evaporation or by sputtering and may consist of a number of layers. The thickness of the cathode material may be from 100 nm to 10,000 nm. The preferred metals are calcium, barium, magnesium, indium, lithium fluoride (LiF), Caesiumfluoride (Csf), Ca(acac) and aluminum. Mixtures or alloys of these materials may also be used.

In a preferred embodiment, the electroluminescent device comprises at least one hole-transporting polymer film and a light-emitting polymer film comprised of the polymer of the invention, arranged between an anode material and a cathode material such that under an applied voltage, holes are injected from the anode material into the hole-transporting polymer film and electrons are injected from the cathode material into the light-emitting polymer films when the device is forward biased, resulting in light emission from the light-emitting layer.

In another preferred embodiment, layers of hole-transporting polymers are arranged so that the layer closest to the anode has the lower oxidation potential, with the adjacent layers having progressively higher oxidation potentials. By these methods, electroluminescent devices having relatively high light output per unit voltage may be prepared.

The term "hole-transporting polymer film" as used herein refers to a layer of a film of a polymer which when disposed between two electrodes to which a field is applied and holes are injected from the anode, permits adequate transport of holes into the emitting polymer. Hole-transporting polymers are typically poly(3,4-ethylenedioxy-thiophene) (PEDOT), PEDOT-PSS (PSS = poly(styrenesulfonic acid), polyaniline (PANI) and polythiophenes. The term "light-emitting polymer film" as used herein refers to a layer of a film of a polymer whose excited states can relax to the ground state by emitting photons, preferably corresponding to wavelengths in the visible range. The term "anode material" as used herein refers to a semi-transparent, or transparent, conducting film with a work function between 4.5 electron volts (eV) and 5.5 eV. Examples are gold, silver, copper, aluminum, indium, iron, zinc, tin, chromium, titanium, vanadium, cobalt, nickel, lead, manganese, tungsten and the like, metallic alloys such as magnesium/copper, magnesium/silver, magnesium/aluminum, aluminum/indium and the like, semiconductors such as Si, Ge, GaAs and the like, metallic oxides such as indium-tin-oxide ("ITO"), ZnO and the like, metallic compounds, and

furthermore, electroconducting polymers such polyacetylene, polypyrrole, polyparaphenylene and the like. Oxides and mixed oxides of indium and tin, and gold are preferred. Most preferred is ITO, especially ITO on glass or plastic as substrate. The term "cathode material" as used herein refers to a conducting film with a work function between 2.5 eV and 4.5 eV. Examples are alkali metals, alkaline earth metals, group 13 elements, silver, and copper as well as alloys or mixtures thereof such as sodium, lithium, potassium, calcium, barium, lithium fluoride (LiF), caesium fluoride (CsF), sodium-potassium alloy, magnesium, magnesium-silver alloy, magnesium-copper alloy, magnesium-aluminum alloy, magnesium-indium alloy, aluminum, aluminum-aluminum oxide alloy, aluminum-lithium alloy, indium, calcium, and materials exemplified in EP-A 499,011, such as electroconducting polymers e.g. polypyrrole, polythiophene, polyaniline, polyacetylene etc. Preferably lithium, calcium, barium, CsF, LiF, magnesium, indium, silver, aluminum, or blends and alloys of the above are used. In the case of using a metal or a metallic alloy as a material for an electrode, the electrode can be formed also by the vacuum deposition method. In the case of using a metal or a metallic alloy as a material forming an electrode, the electrode can be formed, furthermore, by the chemical plating method (see for example, Handbook of Electrochemistry, pp 383-387, Mazuren, 1985).

As methods for forming said thin films, there are, for example, the vacuum deposition method, the spin-coating method, the casting method, the Langmuir-Blodgett ("LB") method, the ink jet printing method and the like. Among these methods, the vacuum deposition method, the spin-coating method, the ink jet printing method and the casting method are particularly preferred in view of ease of operation and cost.

In the case of forming the layers by using the spin-coating method, the casting method and ink jet printing method, the coating can be carried out using a solution prepared by dissolving the composition in a concentration of from 0.0001 to 90% by weight in an appropriate organic solvent such as benzene, toluene, xylene, chlorobenzene, tetrahydrofurane, methyltetrahydrofurane, N,N-dimethylformamide, chloroform, dichloromethane, dimethylsulfoxide and the like. The polymers should be completely soluble in the employed solvents.

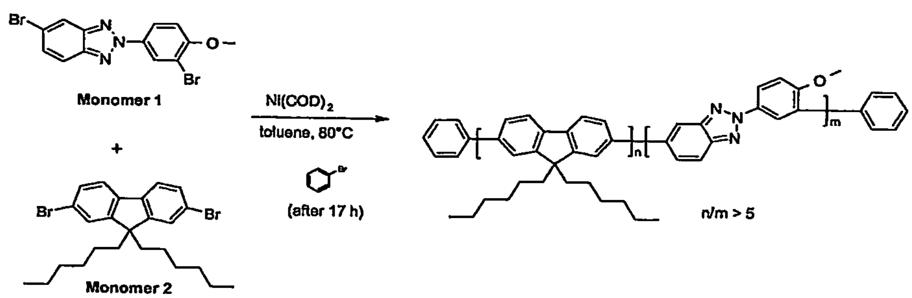
The organic EL device of the present invention has significant industrial values since it can be adapted for a flat panel display of an on-wall television set, a flat light-emitting device, a light source for a copying machine or a printer, a light source for a liquid crystal display or counter, a display signboard and a signal light. The polymers and compositions of the

present invention can be used in the fields of an organic EL device, a photovoltaic device, an electrophotographic photoreceptor, a photoelectric converter, a solar cell, an image sensor, and the like.

The following examples are included for illustrative purposes only and do not limit the scope of the claims. Unless otherwise stated, all parts and percentages are by weight.

Examples

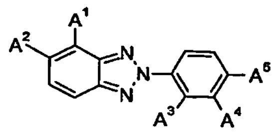
Example 1



Bis(1,5-cyclooctadiene)nickel(0) (2.0 g, 7.27 mmol) and 2,2'-bipyridyl (1.14 g, 7.27 mmol) are dissolved in anhydrous toluene (7.0 ml) and stirred at 80°C for 1 hour under an argon atmosphere in the dark. Monomer 1 (0.23 g, 0.60 mmol) and 2,7-dibromo-9,9-dihexylfluorene (Monomer 2) (1.50 g, 3.05 mmol) are dissolved in anhydrous toluene (7.0 ml) and purged thoroughly with argon, then added to the solution of Ni complex and stirred at 80°C for 17 hours under argon in the dark. Anhydrous toluene (7.0 ml) is added and the reaction allowed to progress a further 5 hours. Bromobenzene (1 ml, 9.5 mmol) is added and the reaction stirred for a further 2 hours. The reaction mixture is poured into stirred methanol/c.$HCl_{(aq)}$ (10:1, 600 ml) and the resulting precipitate is stirred for 30 minutes and collected by filtration. The precipitate is redissolved in toluene (80 ml) and the precipitation repeated in acidic methanol. The precipitate is redissolved in chloroform (80 ml) and passed through a plug of silica, then washed through with chloroform (5 × 100 ml). The combined chloroform phases are concentrated to *ca.* 80 ml and precipitated in stirred methanol (600 ml) and stirred for 30 minutes. The polymer is collected by filtration and dried. 0.674 g; 58% recovery of material: M_W = 650,000, P_D = 2.21 (GPC, PS standards).

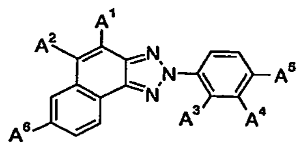
The polymerisation protocol in Example 1 may be used to produce either high M_W homopolymers or high M_W statistical (random) co-polymers from the following monomer families:

Monomer 1:



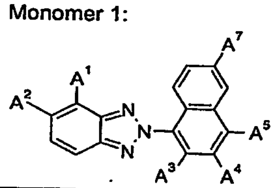
	A^1	A^2	A^3	A^4	A^5	Monomer 2
1	H	Br	H	Br	OMe	2,7-dibromo-9,9-dihexylfluorene
2	H	Br	OMe	H	Br	2,7-dibromo-9,9-dihexylfluorene
3	H	Br	H	H	Br	2,7-dibromo-9,9-dihexylfluorene
4	H	Br	H	Br	OMe	2,7-dibromo-9,9-di(2'-ethylhexyl)fluorene
5	H	Br	OMe	H	Br	2,7-dibromo-9,9-di(2'-ethylhexyl)fluorene
6	H	Br	H	H	Br	2,7-dibromo-9,9-di(2'-ethylhexyl)fluorene
7	H	Br	H	Br	OMe	2,7-dibromo-9,9-diheptylfluorene
8	H	Br	OMe	H	Br	2,7-dibromo-9,9-diheptylfluorene
9	H	Br	H	H	Br	2,7-dibromo-9,9-diheptylfluorene
10	H	Br	H	Br	OMe	2,7-dibromo-9,9-dioctylfluorene
11	H	Br	OMe	H	Br	2,7-dibromo-9,9-dioctylfluorene
12	H	Br	H	H	Br	2,7-dibromo-9,9-dioctylfluorene
13	H	Br	H	Br	OMe	4,4'-dibromo-2,2'-dihexylbiphenyl
14	H	Br	OMe	H	Br	4,4'-dibromo-2,2'-dihexylbiphenyl
15	H	Br	H	H	Br	4,4'-dibromo-2,2'-dihexylbiphenyl
16	H	Br	H	Br	OMe	1,4-dihexyloxy-2,5-dibromophenyl
17	H	Br	OMe	H	Br	1,4-dihexyloxy-2,5-dibromophenyl
18	H	Br	H	H	Br	1,4-dihexyloxy-2,5-dibromophenyl
19	H	Br	H	Br	OMe	1,4-di(2'-ethylhexyl)oxy-2,5-dibromophenyl
20	H	Br	OMe	H	Br	1,4-di(2'-ethylhexyl)oxy-2,5-dibromophenyl
21	H	Br	H	H	Br	1,4-di(2'-ethylhexyl)oxy-2,5-dibromophenyl
22	H	Br	H	Br	OMe	1,4-dioctyloxy-2,5-dibromophenyl
23	H	Br	OMe	H	Br	1,4-dioctyloxy-2,5-dibromophenyl
24	H	Br	H	H	Br	1,4-dioctyloxy-2,5-dibromophenyl

Monomer 1:



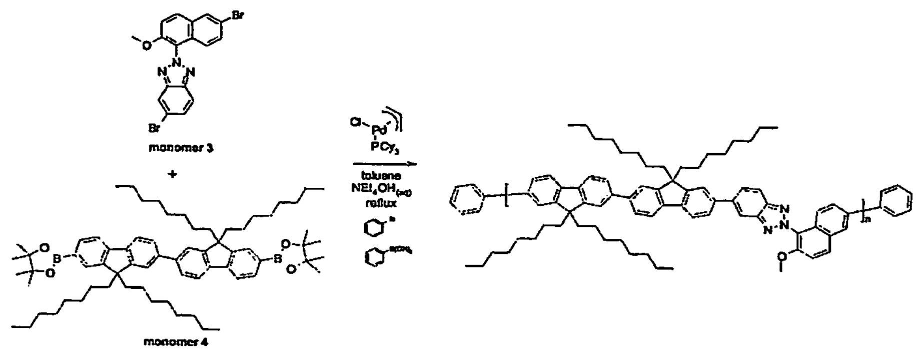
	A^1	A^2	A^3	A^4	A^5	A^6	Monomer 2
25	H	H	H	Br	OMe	Br	2,7-dibromo-9,9-dihexylfluorene
26	H	H	H	H	Br	Br	2,7-dibromo-9,9-dihexylfluorene
27	H	Br	H	Br	OMe	H	2,7-dibromo-9,9-dihexylfluorene
28	H	Br	H	H	Br	H	2,7-dibromo-9,9-dihexylfluorene
29	H	Br	H	H	Br	H	2,7-dibromo-9,9-dioctylfluorene
30	H	H	H	Br	OMe	Br	2,7-dibromo-9,9-dioctylfluorene
31	H	H	H	H	Br	Br	2,7-dibromo-9,9-dioctylfluorene
32	H	Br	H	Br	OMe	H	2,7-dibromo-9,9-dioctylfluorene

Monomer 1:



	A^1	A^2	A^3	A^4	A^5	A^7	Monomer 2
33	H	Br	H	H	Br	H	2,7-dibromo-9,9-dihexylfluorene
34	H	Br	OMe	H	H	Br	2,7-dibromo-9,9-dihexylfluorene
35	H	Br	H	H	Br	H	2,7-dibromo-9,9-di(2'-ethylhexyl)fluorene
36	H	Br	OMe	H	H	Br	2,7-dibromo-9,9-di(2'-ethylhexyl)fluorene
37	H	Br	H	H	Br	H	2,7-dibromo-9,9-dioctylfluorene
38	H	Br	OMe	H	H	Br	2,7-dibromo-9,9-dioctylfluorene

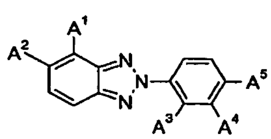
Example 2



Monomer 3 (1.0 g, 2.31 mmol) and monomer 4 (2.38 g, 2.31 mmol) are suspended in toluene (15 ml) and purged by bubbling argon through for 10 minutes. Palladium catalyst (1 mol%) is added and the toluene phase purged for a further 10 minutes. Tetraethylammonium hydroxide (20% aq. solution; 8 ml) is added and the whole heated to reflux for 20 hours. Bromobenzene (0.2 ml) is added and the reaction allowed to proceed for a further hour, then phenylboronic acid is added and the reaction stirred for another hour. On cooling the reaction mixture is diluted with toluene (20 ml) and poured into acidic methanol (10 ml 32% $HCl_{(aq)}$ in 500 ml methanol) and filtered. The pale solid is redissolved in toluene (100 ml) and stirred vigorously with an aqueous solution of disodium EDTA (5%, 200 ml) for 1 hour. The toluene phase is separated, concentrated to *ca.* 50 ml and precipitated in methanol (400 ml), filtered and dried.

The polymerisation in Example 2 may be used to produce either homopolymers or alternating copolymers from the following monomer families:

Monomer 3:

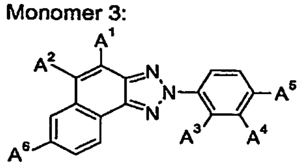


	A^1	A^2	A^3	A^4	A^5	Monomer 4
39	H	Br	H	Br	OMe	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene
40	H	Br	OMe	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene

41	H	Br	H	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene
42	H	Br	H	Br	OMe	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(2'-ethylhexyl)fluorene
43	H	Br	OMe	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(2'-ethylhexyl)fluorene
44	H	Br	H	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(2'-ethylhexyl)fluorene
45	H	Br	H	Br	OMe	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-diheptylfluorene
46	H	Br	OMe	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-diheptylfluorene
47	H	Br	H	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-diheptylfluorene
48	H	Br	H	Br	OMe	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene
49	H	Br	OMe	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene
50	H	Br	H	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene
51	H	Br	H	Br	OMe	4,4'-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-dihexylbiphenyl
52	H	Br	OMe	H	Br	4,4'-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-dihexylbiphenyl
53	H	Br	H	H	Br	4,4'-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-dihexylbiphenyl
54	H	Br	H	Br	OMe	1,4-dihexyloxy-2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl
55	H	Br	OMe	H	Br	1,4-dihexyloxy-2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl
56	H	Br	H	H	Br	1,4-dihexyloxy-2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl
57	H	Br	H	Br	OMe	1,4-di(2'-ethylhexyl)oxy-2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl
58	H	Br	OMe	H	Br	1,4-di(2'-ethylhexyl)oxy-2,5-di(4,4,5,5-tetramethyl-

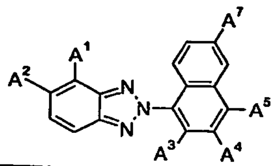
						1,3,2-dioxaborolan-2-yl)phenyl
59	H	Br	H	H	Br	1,4-di(2'-ethylhexyl)oxy-2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl
60	H	Br	H	Br	OMe	1,4-dioctyloxy-2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl
61	H	Br	OMe	H	Br	1,4-dioctyloxy-2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl
62	H	Br	H	H	Br	1,4-dioctyloxy-2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl

Monomer 3:



	A^1	A^2	A^3	A^4	A^5	A^6	Monomer 4
63	H	H	H	Br	OMe	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene
64	H	H	H	H	Br	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene
65	H	Br	H	Br	OMe	H	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene
66	H	Br	H	H	Br	H	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene
67	H	Br	H	H	Br	H	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene
68	H	H	H	Br	OMe	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene
69	H	H	H	H	Br	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene
70	H	Br	H	Br	OMe	H	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene

Monomer 3:



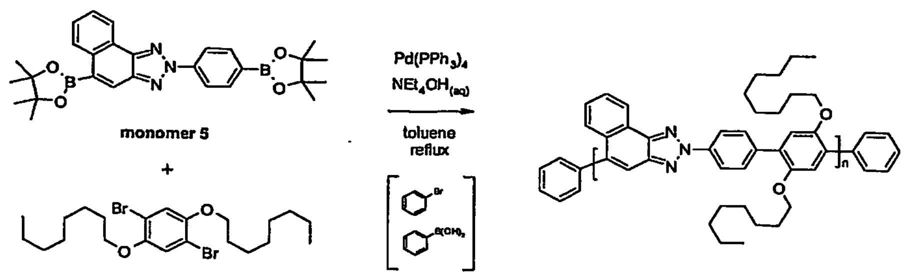
	A^1	A^2	A^3	A^4	A^5	A^7	Monomer 4
71	H	Br	H	H	Br	H	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene
72	H	Br	OMe	H	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene
73	H	Br	H	H	Br	H	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(2'-ethylhexyl)fluorene
74	H	Br	OMe	H	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(2'-ethylhexyl)fluorene
75	H	Br	H	H	Br	H	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene
76	H	Br	OMe	H	H	Br	2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene

Application Example 1

The ITO-glass used for device fabrication is 1 square inch with a nominal sheet resistance of 12 ohm/square. The ITO is patterned by photolithography and etching, then cleaned with water, solvents and finally by exposure to RF-plasma. The PEDOT-PSS (PEDOT = poly(3,4-ethylenedioxy-thiophene), PSS = poly(styrenesulfonic acid)) layer is spin-coated from aqueous dispersion as aquired from Bayer Corporation and baked at 200°C for 30 minutes, such that the final layer thickness was 40 nm. Polymer 67 is spin-coated from toluene solution such that the layer thickness is 80 nm. Calcium (20 nm) and aluminium (70 nm) are thermally deposited in a vacuum chamber. The patterning of ITO and cathode creates 8 active devices of area 4 mm^2.

The devices exhibit a turn-on voltage (luminance > 1 cd/m^2) of 7.4 V, reaching a peak efficiency of 0.012 cd/A.

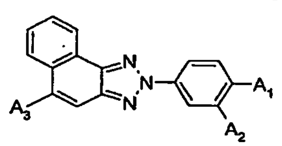
Example 3

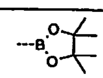
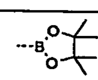
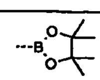
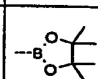


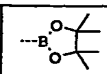
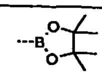
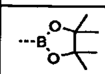
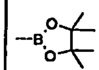
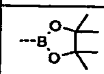
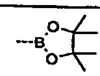
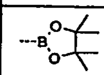
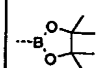
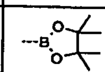
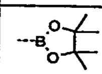
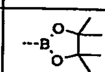
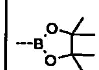
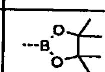
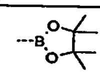
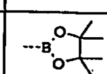
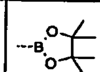
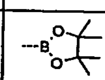
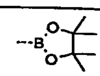
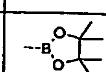
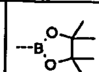
Monomer **5** (1.58g, 3.18 mmol) and monomer **6** (1.57 g, 3.18 mmol) are dissolved in toluene (22 ml) and purged by bubbling argon through for 10 minutes. Palladium catalyst (1 mol%) is added and the toluene phase purged for a further 10 minutes. Tetraethylammonium hydroxide (20 % aq. solution; 12 ml) is added and the whole heated to reflux for 20 hours. Bromobenzene (0.2 ml) is added and the reaction allowed to proceed for a further hour, then phenylboronic acid is added and the reaction stirred for another hour. On cooling the reaction mixture is diluted with toluene (20 ml) and poured into methanol (10 ml 32 % $HCl_{(aq)}$ in 500 ml methanol) and filtered. The pale solid is redissolved in toluene (100 ml) and stirred vigorously with an aqueous solution of disodium EDTA (5 %, 200 ml) for 1 hour. The toluene phase is separated, concentrated to *ca.* 50 ml and precipitated in methanol (400 ml), filtered and dried to yield 1.6 g polymer (85 % recovery).

The polymerisation in Example 3 may be used to produce either homopolymers or alternating copolymers from the following monomer families:

Monomer 5:



	A^1	A^2	A^3	Monomer 6
77			H	1,4-dibromo-2,5-bishexyloxybenzene
78		H		1,4-dibromo-2,5-bishexyloxybenzene

79			H	1,4-dibromo-2,5-bisheptyloxybenzene
80		H		1,4-dibromo-2,5-bisheptyloxybenzene
81			H	1,4-dibromo-2,5-bisoctyloxybenzene
82		H		1,4-dibromo-2,5-bisoctyloxybenzene
83			H	2,6-dibromo-1,5-hexyloxynaphthalene
84		H		2,6-dibromo-1,5-bishexyloxynaphthalene
85			H	2,6-dibromo-1,5-bisheptyloxynaphthalene
86		H		2,6-dibromo-1,5-bisheptyloxynaphthalene
87			H	2,6-dibromo-1,5-bisocttyloxynaphthalene
88		H		2,6-dibromo-1,5-bisocttyloxynaphthalene

Application Example 2

The ITO-glass used for device fabrication is 1 square inch with a nominal sheet resistance of 12 ohm/square. The ITO is patterned by photolithography and etching, then cleaned with water, solvents and finally by exposure to RF-plasma. The PEDOT-PSS layer is spin-coated

from aqueous dispersion as aquired from Bayer Corporation and baked at 200°C for 30 minutes, such that the final layer thickness is 100 nm. Polymer 67 is spin-coated from toluene solution such that the layer thickness is 80 nm. Barium (5 nm) and aluminium (100 nm) are thermally deposited in a vacuum chamber. The patterning of ITO and cathode creates 8 active devices of area 4 mm^2.

The devices exhibit a turn-on voltage (luminance > 1 cd/m^2) of 3.6 V, reaching a peak efficiency of 0.61 cd/A.

Application Example 3

The ITO-glass used for device fabrication is 1 square inch with a nominal sheet resistance of 12 ohm/square. The ITO is patterned by photolithography and etching, then cleaned with water, solvents and finally by exposure to RF-plasma. The PEDOT-PSS layer is spin-coated from aqueous dispersion as aquired from Bayer Corporation and baked at 200°C for 30 minutes, such that the final layer thickness is 100 nm. Polymer 67 is spin-coated from toluene solution such that the layer thickness is 80 nm. Lithium fluoride (5 nm), calcium (10nm) and aluminium (200 nm) are thermally deposited in a vacuum chamber. The patterning of ITO and cathode creates 8 active devices of area 4 mm^2.

The devices exhibit a turn-on voltage (luminance > 1 cd/m^2) of 3.7 V, reaching a peak efficiency of 1.41 cd/A.

Application Example 4

The ITO-glass used for device fabrication is 1 square inch with a nominal sheet resistance of 12 ohm/square. The ITO is patterned by photolithography and etching, then cleaned with water, solvents and finally by exposure to RF-plasma. The polyaniline (PANI) layer is spin-coated such that the final layer thickness is 100 nm. Polymer 67 is spin-coated from toluene solution such that the layer thickness is 80 nm. Lithium fluoride (5 nm), calcium (10nm) and aluminium (200 nm) are thermally deposited in a vacuum chamber. The patterning of ITO and cathode creates 8 active devices of area 4 mm^2.

The devices exhibit a turn-on voltage (luminance > 1 cd/m^2) of 3.8 V, reaching a peak efficiency of 1.39 cd/A.